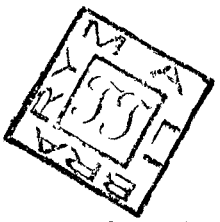
STUDIES ON LESS FAMILIAR CYANIDE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

By
RAIS AHMAD KHAN

DEPARTMENT OF CHEMISTRY
Aligarh Muslim University,
Aligarh. (India)

January, 1974



SUMMARY

Nearly all transition metals other than lanthanides and actinides form well defined cyanides or complex cyanides. Some of these (e.g. the complexes of Fe, Ag and Au) have been recognized as stable species for more than a century. Nevertheless it is only during the past two decades that a systematic investigation of cynaide ions as a ligand in transition metal chemistry has been persued intensively. Increasing attention has been towards the chemistry of molybdenum and tungsten compounds because of their chemical interest and their industrial and biological uses.

Much work has been done on octacyanomolybdates (IV & V) in our laboratory and recently a systematic work has been started on oxo-hydroxocyanomolybdates (IV) and tungstates (IV). Such types of work seems to have drawn little attention from the previous workers in this field. It seems that the experimental difficulties coming in their preparation and purification and the fact that these compounds undergo hydrolytic transformation and are susceptible to light might have been the main obstacles.

The Polarographic behaviour of tripotassium oxo-hydroxo-tetracyanomolybdate (IV), $K_3\left[Mo^{IV}\,O(OH)(CN)_4\right].2H_2O$ (referred to herein as TCM) and tetrapotassium dioxo-tetracyanotungstate(IV) $K_4\left[W^{IV}O_2\,(CN)_4\right].6H_2O$ (referred to herein as TCT) was studied.

These complexes were found to be oxidised step-to-step to the hexavalent state at the dropping mercury electrode in aqueous medium in the presence of 0.1 M KNO_3 and 0.01% gelatin. The resulting molybdate (VI) and tungstate (VI) complex is presumed to be hexa-coordinated $\left[Mo^{VI}\ O(OH)(CN)_4\right]^{-1}$ and $\left[W^{VI}\ O_2(CN)_4\right]^{2-}$ like the original molybdate(IV) and tungstate (IV) complex, and the electrode process can be given as :

$$\left[Mo^{IV}\ O(OH)(CN)_4\right]^{3-} \xrightarrow{e} \left[Mo^{V}\ O(OH)(CN)_4\right]^{2-} \xrightarrow{e} \left[Mo^{VI} O(OH)(CN)_4\right]^{-1}$$

$$\left[W^{IV}O_2(CN)_4\right]^{4-} \xrightarrow{e} \left[W^{V}O_2(CN)_4\right]^{3-} \xrightarrow{e} \left[W^{VI}O_2(CN)_4\right]^{2-}$$

in which no chemical reaction seems to be appreciably involved. Thus, throughout the oxidation, the complexes are considered not to undergo any structural change. The effect of depolarizer concentration, drop-time and temperature was studied with a view to establish the characteristics of the waves.

Both the ions, oxo-hydroxotetracyanomolybdate(IV), $\left[Mo\ O(OH)(CN)_4\right]^{3-}$ and dioxo-tetracyanotungstate(IV), $\left[WO_2\ (CN)_4\right]^{4-}$, produce two anodic waves in 0.1 M KNO_3. The reversibility of the electrode reaction was tested by plotting log $i_{d-i/1}$ vs. $E_{d.e}$. The log plot analysis show that the first step oxidation is reversible and the second one is irreversible in the case of former ion, while the oxidation steps are of reverse order in the case of latter ion. The linearity of the

wave heights with depolariser concentration for TCM and TCT show that the values of $i_{d/c}$ and I are constant with in the experimental error. The plot between the wave heights and depolarizer concentration of both the ions pass through origin. The half wave potential of both the waves were found to be independent of depolarizer concentration. It thus provides a rapid and precize method for polarographic determination of TCM and TCT concentration. The diffusion currents of the first as well as second steps for TCM and TCT were found to be proportional to the square root of mercury pressure. The values of $i_{d/h^{\frac{1}{2}}_{corr.}}$ were constant irrespective of the mercury pressure. This shows that heights of both the waves of TCM and TCT is diffusion-controlled. Above 35°C for TCM and above 10°C for TCT, the current values are seen to deviate from the straight lines of the plot; the current increases remarkably with temperature, indicating a kinetically-controlled characteristics. This may be attributed to the probable disruption of the molybdate(VI) and tungstate (VI) complex formed in solution. Below 35°C and 10°C the current values of both the waves were linear with temperature for TCM and TCT respectively.

The kinetic parameters for the irreversible processess have been evaluated for gaining information about their electrochemical behaviours at the dropping mercury electrode.

The dissociation constants of tetracyanooxohydroxomolybdic acid $H_3[Mo\ O(OH)(CN)_4]$ has been obtained in the temperature range 25-50°C from the pH-titration curve of its tripotassium salt against Hcl. Potentiometric titrations of tripotassium oxo-hydroxotetracyanomolybdate(IV) with Hcl showed two inflection points. The first inflection occured at a pH between 6.65 to 7.5. This corresponds to the formation of dibasic complex $[Mo\ (OH)_2(CN)_4]^{2-}$ due to the addition of one proton (H^+) to $[Mo\ O(OH)(CN)_4]^{3-}$. The pH at the mid point of the first segment is taken to be equal to pK'_3. When 3 equivalents of (H^+) were added, a second inflection points lying at a pH between 2.75 to 5.5 occured. The second equivalence point was not as sharp as the first one. The pH at the mid point of the second segment is taken to be equal to pK'_2. The pK'_3 and pK'_2 values have been dtermined for a wide range of temperature and ionic strength. Thermodynamic quantities such as $\triangle G^o$, $\triangle H^o$, $\triangle S^o$ and $\triangle C_p^o$ have been calculated at 30°C.

The dissociation constant of tetracyanodioxotungstic acid $H_4[WO_2\ (CN)_4]$, has been studied in the temperature range 30-50°C from pH-titrations curve of its tetra potassium salt against Hcl. The potentiometric titrations of tetra-potassium dioxotetracyanotungstate(IV) with Hcl show no sharp inflection points. On addition of one mole of (H^+) to the complex ion, in general, pH changes from 11.5 to 9.85. Further.

this change is quite gradual and corresponds to the formation of $K_3\left[WO(OH)(CN)_4\right]$. The hydrolysibility difference between $\left[WO_2(CN)_4\right]^{4-}$ and $\left[WO(OH)(CN)_4\right]^{3-}$ is such that it does not allow a sharp change in pH. Further addition of one mole of (H^+) corresponds to the formation of dibasic complex $\left[W(OH)_2(CN)_4\right]^{2-}$. Again no sharp change in pH occurs in this case as well. Further addition of one equivalent of (H^+) results in a small change in pH, probably due to the formation of $\left[W(OH)_2(CN)_3\right]^{-1}$. At about 3.35 equivalents of (H^+), a fairly sharp change in pH occurs. This seems to be correspond to the formation of $W(OH)(CN)_2$. This inflection occurs at 3.35 equivalents instead of 4 equivalents of (H^+) due to the incomplete conversion of $\left[W(OH)_2(CN)_3\right]^{-1}$ into the inner complex $W(OH)_2(CN)_2$. As the inflection point occurs at 3.5 equivalents instead of 4, from this titration curve one can not get the exact value of dissociation constant.

The composition of Ag, Cu and Ni ammine complexes with tripotassiumoxohydroxotetracyanomolybdate(IV) has been studied by potentiometric and conductometric methods. Both, (direct TCM as the titrant) and (reverse metal ammine as the titrant), titrations were done. The stoichiometric ratio of 1:4 for TCM to silver ammine results into the formation of a soluble complex $Ag_2\left[Mo^{VI}O_2(CN)_4\right]$. The reaction seems to proceed as follows :

$$2\left[Ag(NH_3)_2\right]^{+}+\left[Mo^{IV}O(OH)(CN)_4\right]^{3-}\longrightarrow\left[Mo^{VI}O(OH)(CN)_4\right]^{-1}+2Ag+4NH_3$$

$$2\left[Ag(NH_3)_2\right]^{+}+\left[Mo^{VI}O(OH)(CN)_4\right]^{-1}\longrightarrow Ag2\left[Mo^{VI}O_2(CN)_4\right]+NH_4^{+}+3NH_3$$

The interaction of TCM and Copper ammine provide enough evidence regarding the composition of complex formed. These titrations indicate the formation of 1:2 and 1:1 complexes during the direct and reverse titrations respectively. The following reaction may be visualized to take place:

$$\left[Cu\ (NH_3)_4\right]^{2+} + \left[Mo^{IV}O(OH)(CN)_4\right]^{3-} \longrightarrow \left[Mo^{VI}O(OH)(CN)_4\right]^{-1} + Cu + 4NH_3 \quad \ldots(1$$

$$\left[Cu\ (NH_3)_4\right]^{2+} + \left[Mo^{VI}O(OH)(CN)_4\right]^{-1} \longrightarrow Cu\left[Mo^{VI}O_2(CN)_4\right] + NH_4^{+} + 3NH_3 \quad \ldots(2$$

The potentiometric as well as conductometric titrations show that the product formed in the 1:1 ratio is unstable in the presence of an excess of ammine and ends up in a 1:2 instead of 1:1 complex. On the other hand, in the reverse titration the product formed according to the reaction seems to be stable in the presence of excess of TCM and hence the titrations indicate the 1:1 end point. The results of potentiometry were also confirmed by conductometry

The reaction between tripotassium oxo-hydroxocyanomolybdate(IV) (TCM) and nickel ammine was carried out by potentiometric and conductometric titrations. These titrations indicate the formation of $Ni\left[Mo^{VI}O_2(CN)_4\right]$. The ratio for (TCM: Ni^{2+}) is 1:2 and the reaction may be represented as follows :

$$\left[Ni(NH_3)_6\right]^{2+} + \left[Mo^{IV}O(OH)(CN)_4\right]^{3-} \longrightarrow \left[Mo^{VI}O(OH)(CN)_4\right]^{-1} + Ni + 6NH_3$$

$$\left[Ni(NH_3)_6\right]^{2+} + \left[Mo^{VI}O(OH)(CN)_4\right]^{-1} \longrightarrow Ni\left[Mo\ O_2(CN)_4\right] + NH_4 + 5NH_3$$

$$2\left[Ni(NH_3)_6\right]^{2+} + \left[Mo^{IV}O(OH)(CN)_4\right]^{-3} \longrightarrow Ni\left[Mo^{VI}O_2(CN)_4\right] + Ni + NH_4^{+} + 11NH_3$$

D E D I C A T E D

T O

My parents and brothers without whose self-sacrifice I would not have had my education.

FAIZ AHMAD KHAN

A C K N O W L E D G E M E N T

I am very pleased to acknowledge my indebtness to my supervisor Dr. M.A. Beg, (Reader) Department of Chemistry, Aligarh Muslim University, Aligarh for the inspiration and able guidance. For rewarding suggestions and advice given to me, I wish to express my grateful thanks to Dr. Kabir-ud-Din.

I am thankful to Professor Wasiur Rahman Head of the Chemistry Department Aligarh Muslim University, Aligarh for providing research facilities in carrying out this work.

Rais Ahmad Khan

RAIS AHMAD KHAN

C O N T E N T S

(Contd.)

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GENERAL INTRODUCTION

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Both, molybdenum and tungsten have a number of oxidation states, and their chemistry is among the most complex of the transition elements. In recent years, both the metals have assumed importance from the commercial as well as chemical and biological point of view. Molybdenum filaments have been proposed for lamps. The metal has been used as an ingredient in the preparation of arc-light electrodes. Some of the molybdenum preparations have been used in photography; in dyeing silks, wool, rubber and leather; in the preparation of blue colours, and for producing red and yellow pottery glazes and glasses. Its various compounds are used as chemical reagents in qualitative tests and quantitative estimations. It is widely used for the preparation of "molybdenum steels" which have found great use in armoury. The greatest use of tungsten is in the preparation of iron or steel alloys for high-speed tools. "High speeds steels which are used to make cutting tools which remain hard even at red heat, contain W and Cr. Tungsten is also extensively used for lamp filaments. The other use is as resistance wire in tungsten arc-lamps, and as resister-wire-wound electric furnaces.

Both molybdenum and tungsten have a wide variety of oxidation states, the lower oxidation states are unstable and reducing in nature. The higher oxidation states (+6) are most stable. Both Mo^{VI} and W^{VI} give tetrahedral oxo anion MoO_4^{2-} whose alkali metal salts are water soluble. Mo^{VI} and W^{VI} give a variety of complexes with organic substances such as sugars, tartaric acid etc. whose structures are not properly known. Interest in such species derives in part from the fact that Mo is thought to be one of the essential elements in biological systems, e.g., in nitrogen-fixing bacteria; there has accordingly been much study of aqueous Mo^{VI} complexes but the precize nature of many of the species is hard to ascertain[1]. The reduction of aqueous Mo^{VI} and W^{VI} species can lead to a variety of oxo species of Mo^{V} and W^{V}. This formation of oxo species with M = O and/or M-O-M bonds is a characteristic property of these elements. While Mo^{V} and W^{V} solutions are usually air sensitive, these states can be stabilized by suitable complexing.

The lower oxidation states of both the metals are easily convertible to the hexavalent state. The other oxidation states have been characterized only in complex ion forms. The chemistry of their complex ions remains very much obscure due to the formation of isopoly and

heteropoly ions. Of these, however, the tetra and pentavalency state cyanide complexes are better characterized.

The first known cyanide complex was Prussian Blue, prepared in 1704 by the German artist Diesbach who heated animal refuse and sodium carbonate together in an iron pot.[2] Subsequent work led to the isolation of potassium ferrocyanide, $K_4[Fe(CN)_6]$.[3] Since then, cyanide complexes of most transition metals have been prepared, as well as simple cyanides of non-transition metals. The CN^- group is capable of stabilising a wide range of stereochemical configurations and metal oxidation states. In unsubstituted cyanide complexes, co-ordination numbers from eight to two and oxidation states from (+5) to (o) are known.

Nearly all transition metals other than lanthanides and actinides form well defined cyanides or complex cyanides. Some of these (e.g. the complexes of Fe, Ag and Au) have been recognized as stable species for more than a century. Nevertheless it is only during the past two decades that a systematic investigation of cyanide ion as a ligand in transition metal chemistry has been persued intensively. In recent years, increasing attention has been paid towards the chemistry of molybdenum and tungsten compounds because

of their chemical interest and their industrial and biological uses.

Much work has been done on octacyanomolybdates(IV,V) in our laboratory[4,5] and recently a systematic work has been started on oxo-hydroxocyanomolybdates(IV) and-tungstates(IV).[6] Such type of work seems to have drawn little attention from the previous workers in this field. It seems that the experimental difficulties coming in their preparation and purification and the fact that these compounds undergo hydrolytic transformation and are susceptible to light might have been the main obstacles. It is for this reason that only few references are available in the existing literature on their physico-chemical properties. Nevertheless, whatever has been done on the various aspects of the problem is worthmentioning.

Special interest is attached to the complex cyanides of molybdenum and tungsten, $R_4[Mo(CN)_8]$ and $R_4[W(CN)_8]$, because fewer cyanides are known of quadrivalent elements and complex cyanides are known only in isolated cases. Moreover the complex salts represent well substantiated examples of a co-ordination number of 8, and the exceptional the complex ions $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ finds a satisfactory explanation in the modern electronic theory

of valency. Undoubtedly, this marked stability associated with the fact that the cyanide units are regularly distributed round the central metallic atom, of which the effective atomic number in the case of molybdenum 54 and of tungsten 86 is that of the higher inert gas.

Collenberg[7] observed that $K_4[R(CN)_8]$ (R=Mo or W) in sun light, decompose and give the usual cynogen test with mercury and silver salts. He further studied the photochemical reaction in alkali solution and found that the reaction velocity was dependent upon the concentration of alkali, being greatest from 0.5N to 1N, and is also greater for Mo than for W compound. According to him, the reaction proceeds as:

$$K_4[R(CN)_8] + Y\ OH^- \underset{KCN}{\overset{light}{\rightleftharpoons}} K_4[R(OH)_y(CN)_{8-y}] + CN^-$$

The alkaline solution of molybdenum compound on standing changes its colour and becomes reddish-brown, then to green, finally to dark blue; while the tungsten compound becomes reddish-brown, then wine-red, and finally reddish-violet.

A much more satisfactory explanation has been given by Bucknall and Wardlaw[8] by considering the effective atomic number of the central atom in the various complex salts

involved in the preparation of the complex cyanides. The salt $K_4[Mo(CN)_8]$ is normally prepared by the interaction of KCN with complex compounds of either tervalent or quinquevalent molybdenum. In the former case the reaction may be conveniently formulated as:

$$K_3MoCl_6 + 8\ KCN + \tfrac{1}{2}\ H_2O + \tfrac{1}{4}\ O\ (air) = K_4[Mo(CN)_8] + 6KCl + KOH$$

The instability of the intermediate $K_3[Mo(CN)_6]$ - a salt as yet unisolated which reverts to the stable $K_4[Mo(CN)_8]$, can be readily appreciated when it is seen that the effective atomic number of molybdenum is only 51, where as in the stable compound it is 54. In the preparation from the complex chlorides of quinquevalent molybdenum, R_2MoOCl_5, the importance of the effective atomic number of the molybdenum in $K_4[Mo(CN)_8]$ is again emphasized. The reaction may be considered as occuring in the following stages:

$$K_2MoOCl_5 + 5\ KCN = K_2MoO(CN)_5 + 5\ KCl$$

$$K_2MoO(CN)_5 + 3KCN + H_2O = K_3[Mo(CN)_8] + 2KOH$$

$$2K_3Mo(CN)_8 + 2KOH = 2K_4[Mo(CN)_8] + H_2O + \tfrac{1}{2}\ O_2$$

The instability of the salt $K_2MoO(CN)_5$ follows as a consequence of the low effective atomic number viz., 49, of the molybdenum atom, whilst the formation of $K_4[Mo(CN)_8]$ from

$K_3[Mo(CN)_8]$ involves a change in effective atomic number from 53 to 54 - a clear proof of the influence of an inert gas structure in determining chemical stability. The inability to oxidize $K_4[Mo(CN)_8]$ to the salt $K_2[Mo(CN)_8]$ of sexavalent molybdenum, with an effective atomic number of 52, is not surprising in view of the experimental evidence that $K_3[Mo(CN)_8]$ functions as an oxidising agent in order to revert to more stable $K_4[Mo(CN)_8]$. This change is readily brought about by light or by the action of heat. Further evidence of the instability of the system $[Mo(CN)_8]^{3-}$ is seen in the rapidity with which, the green complex salt $Cu_3[Mo(CN)_8]_2$ reverts to the purple $Cu_2[Mo(CN)_8]$.

Rosenheim and Dehn[9] were the first to synthesize the octacyanotungstates. Silicotungstic acid was used as the starting material. It was dissolved in fuming HCl and a 20% solution of it was subjected to electrochemical reduction until the trivalent tungsten compound was formed:

$$H_8[Si(W_2O_7)_6] + 54\ HCl + 36\ e = 6H_3[W_2Cl_9] + H_2SiO_3 + 42\ H^+$$

The solution was then subjected to almost complete neutralization with KOH:

$$H_3[W_2Cl_9] + 3KOH = K_3[W_2Cl_9] + 3H_2O$$

Then, after the addition of KCN, the octacyanotungstate complex was formed in the solution:

$$K_3\left[W_2^{III}Cl_9\right] + 16\ KCN + H_2O + \tfrac{1}{2}\ O_2 = 2K_4\left[W^{IV}(CN)_8\right] + 9KCl + 2KOH$$

The isolation of this compound in a pure state was accomplished in a course of four operations. Initially, a rather impure cadmium salt of the complex was precipitated in the presence of acetic acid. This precipitate was dissolved in ammonia and a crystalline ammine salt was separated out. Then this ammine was converted into an aquo compound with the help of sulphuric acid. Finally a potassium salt of the complex was obtained by the action of potassium carbonate. The course of the reactions were as follows:

$$2Cd^{2+} + \left[W(CN)_8\right]^{4-} + aq = Cd_2\left[W(CN)_8\right]\cdot 8H_2O$$

$$Cd_2\left[W(CN)_8\right]\cdot aq + 6NH_3 = \left[Cd(NH_3)_3\right]_2\left[W(CN)_8\right]\cdot 2H_2O$$

$$\left[Cd(NH_3)_3\right]_2\left[W(CN)_8\right] + 3H_2SO_4 + aq = Cd_2[W(CN)_8]\cdot 8H_2O + 3(NH_4)_2SO_4.$$

$$Cd_2\left[W(CN)_8\right]\cdot 8H_2O + 2K_2CO_3 = K_4\left[W(CN)_8\right]\cdot 2H_2O + 2CdCO_3 + aq.$$

In 1915, Rosenheim and Dehn[10] put forward a second method for the synthesis of octacyanotungstates, starting from the thiocyanogen compounds of pentavalent tungsten.

During the reaction of hydrochloric acid on sodium paratungstate solution and sodium thiocyanate, tungsten is reduced to the pentavalent state because of thiocyanic acid. After the addition of pyridine, the compound $W^{V}(OH)_2(CNS)_3 \cdot 2C_5H_5N$ was liberated. By the action of KCN on this compound, the solution acquires a blue colour initially, which transforms into a dark yellow colour on heating, because of the formation of octacyanotungstate. Purification and isolation of compound were effected using cadmium salt as in the first method.

Due to certain differences in the above two methods (namely, the use of fuming HCl in the first method and the formation of a considerable quantity of black resinous substance in the second method) Olsson[11] put forward an improved method for the synthesis. The first reaction in this method is the preparation of the complex chloride of the trivalent W^{III}. Metallic tin in the presence of hydrochloric acid was used as the reducing agent for tungstic acid;

$$2H_2WO_4 + 3Sn + 15\ HCl = H_3\left[W_2Cl_9\right] + 3SnCl_2 + 8H_2O$$

After liberating the potassium salt of the monochloroditungstate complex by reaction with potassium cyanide according to the equation:

$$K_3W_2^{III}Cl_9 + 16KCN + H_2O + \tfrac{1}{2}\ O_2 = 2K_4\left[W(CN)_8\right] + 9KCl + 2KOH$$

Potassium octacyanatungstate was obtained. Its liberation from the solution was effected by crystallization and precipitation with 95% alcohol.

Mikhalevich and Litvinchuk[12] developed a new method for the synthesis of octacyanotungstate. They reduced electrochemically a solution of ammonium-para-tungstate in the presence of ammonium oxalate and oxalic acid at a current density of 0.5 amp./cm^2 and obtained an oxalate complex of composition $(NH_4)_2O_2W_2O_3(COO.COOH)_2 \cdot 4H_2O$ and also the tungstyl hydroxide $WO(OH)_3$. By the action of an excess of potassium cyanide on $WO(OH)_3$ in an acid medium and in the presence of carbondioxide, potassium octacyanotungstate, $K_4\left[W^{IV}(CN)_8\right] \cdot 2H_2O$, is formed:

$$2WO(OH)_3 + KCN + CO_2 = K_4\left[W(CN)_8\right] + K_2WO_4 + 3H_2O.$$

The photochemical or thermal decompostion of aqueous octacyanomolybdate(IV) and octacyanotungstate(IV) in neutral or alkaline solution produces a series of aquo-or hydroxocomplexes. Irradiation of these solutions by light of wave-lengths near the ultraviolet changes the colour rapidly from yellow to red and then, slowly, to blue(Mo) or violet(W) via green.[13-19] An increase in pH takes place as the decomposition proceeds.[20,21] From the red stage the

colour reversal can be achieved by allowing the solution to stand in the dark or by heating, the reversal being accompanied by a decrease in the pH.[20-22] This reversal can also be achieved by the addition of base[17,22]

Hydroxocyanomolybdates

The complex hydroxocyanide of molybdenum was first prepared by Van der Heide and Hofmann.[23] They reduced an acid solution of MoO_3 with KI, removed excess of iodine, treated the solution subsequently with KCN and KOH and obtained red crystals to which they assigned the formula $4KCN.MoO_2.10H_2O$.

Rosenheim, Garfunkel and Kohn[24] treated $(NH_4)_2MoOCl_5$ or $Mo(OH)_2(CNS)_3(C_5H_5N)_2$ with KCN subsequently added KOH and obtained a similar compound.

Collenberg[13] isolated reddish-violet needle shaped crystals during the decomposition of octacyanomolybdate(IV) in sun light in the presence of KOH. They assigned the formula $K_4Mo(OH)_3(CN)_5\ 3H_2O$ or $6H_2O$, but this has recently been shown to be incorrect.[22,25-27]

Bucknall and Wardlaw[8] gave another method for the preparation of hydroxomolybdocyanides. They reacted molybdenyl hydroxide, $MoO(OH)_3$, with the theoretical amount

of KCN and obtained a blue aqueous solution, from which red crystals were precipitated of KOH.

They formulated this red compound as $K_4[Mo(OH)_4(CN)_4] \cdot 4H_2O$. The fact that the red cyanide becomes blue on dehydration and yet yielded a blue aqueous solution seems to depend on equilibrium:

$$K_4[Mo(OH)_4(CN)_4] \cdot 4H_2O \rightleftharpoons K_3[Mo(OH)_3(CN)_4H_2O] \cdot 2H_2O + KOH + H_2O$$

It was noticed that the red colour of the complex cyanide is attained only in the presence of concentrated KOH, and on the removal of free alkali, the pure complex salt becomes bluish-violet. It appears probable, therefore, that on dehydration and on dissolution in water, a decomposition takes place in accordance with the above equation.

Bucknall and Wardlaw[8] also studied its numerous interesting properties. For example, excess of KCN changed the red into yellow octacyanide according to the following reaction:

$$[Mo(OH)_4(CN)_4]R_4 + 4\,RCN \rightleftharpoons [Mo(CN)_8]R_4 + 4ROH$$

$$[MoO_2(CN)_4]R + 4RCN \rightleftharpoons [Mo(CN)_8]R_4 + 2R_2O$$

The red complex gave a blue solution from which KOH reprecipitated the original cyanide. Addition of alcohol

to blue aqueous solution resulted in the precipitation of a blue solid, which on further dissolution in water, and reprecipitation with alcohol give a blue compound having the formula $K_3[Mo(OH)_3(CN)_4H_2O]\cdot 2H_2O$. Excess of KCN changed it into the octacyanide $K_4[Mo(CN)_8]$.

Golding and Carrington[28] successfully prepared the red cyanide and gave it the same formula as Wardlaw. Steele[29] also attempted to prepare the red and blue complexes, and obtained a new brown compound, $K_4[MoO_2(CN)_4]$, by refluxing a solution of KCN and MoO_3.

Jakob and Turkiewicz[30] obtained the red cyanide when 100 grams of ammonium molybdate was dissolved in 100 c.c. of HCl, reduced with 17 grams of $N_2H_4\cdot HCl$ and treated the resulting $MoO(OH)_3$ with 200 grams of KCN and 30 grams of KOH. The hydrolysis of this red hydroxocyanide proceeds in two steps and was enhanced by H^+ ions, the products being $[Mo(CN)_4(OH)_3\ H_2O]^{3-}$ and $[Mo(CN)_4(OH)_2]^{2-}$.[30]

There is some disagreement in the literature as to the nature of red intermediate formed in the photolysis of aqueous solution of $K_4[Mo(CN)_8]$. Jakob et.al.[17,31] on the basis of the existence of isolation and preparation of

red complexes of general formula $M_2[Mo(CN)_8R_2]\cdot XH_2O$ (where M = Cd(II) or Mn(II); R = H_2O, NH_3, N_2H_4) suggested that the red intermediate is probably a deca coordinate with D_4d based geometry ("supper-complex" as they called it) $[Mo(CN)_8(H_2O)_2]^{4-}$ complex anion. The aqueous solutions of $M_2[Mo(CN)_8R_2]\cdot XH_2O$ are stable in dark but hydrolyse in light to the blue cyanide, to which they assigned the formula $K_2[Mo(CN)_4(OH)_2]$.

Adamson and Perumareddi[19] have shown that on photolysis of $K_4[Mo(CN)_8]$ in 363 nm light gave a final blue product. It was precipitated by fractional precipitation with ethyl alcohol. It was diamagnetic and was proposed to have the formula $K_3[Mo(CN)_4(OH)_3(H_2O)]$.

Similar conclusions were reached by Carassiti and coworkers[14-16] and independently by Perumareddi.[32]

Gray and Spence[33] studied the photoreduction of $[Mo(CN)_8]^{3-}$ to red $[Mo(CN)_7(H_2O)]^{3-}$. In basic solution $[Mo(CN)_7(H_2O)]^{3-}$ is first formed, but this undergoes fast hydrolysis to blue $[Mo(CN)_4O(OH)]^{3-}$. Evidence for various dark reactions was also obtained.

Jakob and Mikhalewicz[30b] reported a number of metal complexes of molybdenum hydroxocyanide and studied their

properties. A blue-purple Cd(II) salt, $Cd(H_2O)_6[Mo(CN)_4(OH)_2]$, was obtained by adding $CdCl_2$ to a solution of $Na_4[Mo(CN)_4(OH)_4] \cdot 12H_2O$ neutralized with 1% acetic acid. Purple Crystals of an ammino salt, $Cd(NH3)_3[Mo(CN)_4(OH)_2]$, were prepared by the interaction of the red alkali salt and ammonical solution of the metal chloride in the presence of NH_4Cl. This red salt was found to be insoluble in water but soluble in concentrated ammonia giving a blue colour. Hot Na_2CO_3 solution decomposed it to NH_3 and $CdCO_3$. An anologous $Mn^{(II)}$ salt, $Mn(H_2O)_6[Mo(CN)_4(OH)_2]$ was also prepared. Addition of $MnCl_2$ and NH_3 to a nearly neutralized solution of $K_4[Mo(CN)_4(OH)_4] \cdot 6H_2O$ precipitated a purple compound, $Mn(NH_3)_2[Mo(CN)_4(OH)_2] \cdot H_2O$. It was found that another salt, richer in NH_3, $Mn(NH_3)_2(NH_4)[Mo(CN)_4(OH)_3] \cdot H_2O$, was formed when ammonia was in an excess. Jakob and Jakob[25] reported to have prepared the same violet $Cd^{(II)}$ salt upon adding Cd^{2+}, NH_4Cl and NH_3 to $K_4[Mo(CN)_4(OH)_4]$ solution.

A good deal of work was carried out on hydroxocyanomolybdate(IV) in this laboratory by Beg and co-workers[6]. A spectrophotometric investigation of the interaction of potassiumaquohydroxocyanomolybdate(IV) with U(VI) and V(IV) revealed the formation of 1:1 complex of reddish-brown and

violet colour respectively. The average values of the formation constant are $(2.96 \pm 0.1)\ 10^3 (7.2 \pm 0.1) 10^4$ and ΔF° are -4.76 and - 6.66 ± 0.01 Kcal/mole at 25° are calculated in the respective cease. Vanadium(IV), $VOSO_4$ solution can be estimated readily by conductometric, potentiometric or amperometric titrations with $K_3[Mo(CN)_4(OH)_3(H_2O)]$. The amperometric titration was carried out at an applied potential of -1.25V vs. saturated calomel electrode in 0.1M KCl containing 0.01% gelation.[6a]

The composition of freshly precipitated Cr, Fe compound was $M[Mo(CN)_4(OH)_3(H_2O)]$ (Where M = $Cr^{(III)}$, $Fe^{(III)}$ whereas the composition of Mn-hydroxocyanomolybdate can be given as $KMn[Mo(CN)_4(OH)_3(H_2O)]$[6]. The redox potential of cyanomolybdate depends on the properties of the coordinating groups. The standard potential for $[Mo(CN)_8]^{3-} + e \rightleftharpoons [Mo(CN)_8]^{4-}$ has been reported as 0.84V in the presence of KCl as stated concentration (0°)[34] or 0.73V at infinite dilution at 25°.[35]

Mikhalevich[36] carried out some experiments to determine the oxidation-potential of hydroxocyanomolybdates and also studied their oxidation-reduction properties. He obtained a value of $E_{Mo^V/Mo^{IV}} = 0.10V$, when $4CN^-$ groups of the octacyanide anion were replaced by $4OH^-$ groups. At pH 13.5 this value becomes 0.76V. The author reported that the

hydroxotetracyanomolybdates possess strong reducing properties and can reduce cations to free metals, partially reduce cations to a lower valency state, reduce non metals to anions, reduce complex substances, and lower the valency of the central atom in anions.

In a detailed study of redox properties of hydroxocyanomolybdate(IV) Beg and coworkers[6] determined the (E^{o}) values for $Mo^{(IV)}$ and $Mo^{(VI)}$ hydroxocyanide complex ion couple in alkaline medium at different ionic strength, temperature and concentration of KOH. The oxidation-reduction mechanism was given as:

$$\left[Mo^{IV}(CN)_4(OH)_3(H_2O)\right]^{3-} \rightleftharpoons \left[Mo^{V}(CN)_4(OH)_3(H_2O)\right]^{2-} + e \rightleftharpoons \left[Mo^{VI}(CN)_4(OH)_3(H_2O)\right]^{-1} + 2e$$

and dependence of (E^{o}) value on KOH concentration was represented as:

$$E\ (OX./red) = E^{o} - RT/nF \ln [OX]/[red]KOH^{0.5}$$

During the hydrolytic transformation of hydroxocyanomolybdates according to the scheme.

$$\left[Mo(CN)_4(OH)_4\right]^{4-} \rightleftharpoons \left[Mo(CN)_4(OH)_3(H_2O)\right]^{3-} \rightleftharpoons \left[Mo(CN)_4(OH)_2(H_2O)_2\right]^{2-}$$

There occurs a significant change in the basicity of the medium as well as the redox potential characteristic of the system. The hydrolysis constants of these tetra,-tri and dihydroxocyano complexes have been determined at 16°c to be 2.8×10^{-2}, 3.4×10^{-6} and 7.9×10^{-9} and also their acid ionization constants as 2.2×10^{-13} and 1.8×10^{-9} and 7.9×10^{-7}, respectively.[18] The acid dissociation constants for $[MoO(OH)(CN)_4]^{3-}$ and $[Mo(OH)_2(CN)_4]^{2-}$ at 25° have again been determined as 2.4×10^{-13} and 1.05×10^{-10}, respectively.[37]

Quite recently, however, several authors[37-39] have presented a variety of persuasive but some what indirect evidence that the red complex ion is not the presumed $[Mo(OH)_4(CN)_4]^{4-}$ ion of the older literature, but is instead the trans form of the octahedral $[MoO_2(CN)_4]^{4-}$ ion. The spectroscopic and other evidence which Lippard et.al., put-forward in favour of the $[MoO_2(CN)_4]^{4-}$ formulation for the red complex, and of the $[MoO(OH)(CN)_4]^{3-}$ for the blue species. They have shown by diffraction, i.r. spectroscopic and chemical evidence to have two oxygen atoms trans to each other. The electronic spectra of these diamagnetic complexes are reported and their visible bands assigned. The spectroscopic studies indicate that the existence of oxygen metal and to a lesser extent to the metal cyanide II-bonding.[41]

Both, the red complex and the blue hydrolytic product thereof, are readily converted into the familiar octacyanomolybdate(IV) speceis by reaction with KCN[8]. With reference to solution chemistry, it is only the blue $[MoO(OH)(CN)_4]^{3-}$, that is important. At low pH the blue complex transforms into a less fully characterized green species to which a tentative formula $[Mo(OH)_2(CN)_4]^{2-}$ has been assigned.

The decided preference of Mo(IV) and oxide oxygen atoms for unhibited double bonding is almost clearly suggested by one outstanding feature of the crystalline structure of Na $K_3MoO_2(CN)_4 \cdot 6H_2O$. Each of the oxygen atom of the complex ion is strongly hydrogen bonded to two water molecules, of the partially hydrated sodium ion, so that transfer of any one of the four protons from a molecule to a complex oxygen atom, a jump of only 0.70A° for the proton would transform the red $[MoO_2(CN)_4]^{4-}$ into the blue $[MoO(OH)(CN)_4]^{3-}$ species.

Hydroxocyanotungstates

The hydroxocyanide complexes of tungsten and molybdenum have close resemblance to one another in many aspects. In this manner, a large number of information is obtained.

Crystalline potassium hydroxotetracyanotungstate was first prepared by Collenberg,[13] by the decomposition of octacyanotungstate(IV) $K_4[W(CN)_8]\cdot 2H_2O$ in direct sun light in alkaline medium. He assigned a formula $K_4[W(OH)_3(CN)_5]\cdot 6H_2O$ to the red hydroxocyanide obtained. But recent work[17,26,27] suggests that this compound, if it exists, is very unstable. Mikhalevich and Litvinchuk[18,42] described a new method the synthesis of hydroxotetracyanotungstate(IV) by electro reduction of ammonium paratungstate in the presence of ammonium oxalate and oxalic acid. After cooling the cathode solution was filtered and neutralized with a low percent ammonia solution. Precipitation of tungstyl hydroxide $WO(OH)_3$ from the cathode solution was done by ammonia. The filtered and washed precipitate of $WO(OH)_3$ was heated in the presence of KCN in an alkaline medium. Dissolution of brown precipitate gave a purple-violet solution. The compound $K_4[W(OH)_4(CN)_4]\cdot 4H_2O$ was isolated in the crystalline form with solid KOH. Mikhalevich and Litvinchuk used $K_3Fe(CN)_6$ for potentiometric estimation of $K_4[W(CN)_4(OH)_4]\cdot 4H_2O$. Measurements of the pH of aqueous solution of hydroxotetracyanotungstate showed that di-, tri-, and tetra substituted forms exist in aqueous solution. The form of the complexes depend on the acidity of the medium.

Three protonation stages being possible before decomposition;[18] e.g.,

$$\underset{\text{brown-yellow}}{\left[W(CN)_4(OH)_4\right]^{4-}} \rightleftharpoons \underset{\text{Lilac}}{W(CN)_4(OH)_3(H_2O)^{3-}} \rightleftharpoons$$

$$\underset{\text{blue}}{\left[W(CN)_4(OH)_2(H_2O)_2\right]^{2-}} \xrightarrow[T>60^\circ]{H^+} \underset{\text{green}}{W(CN)_2(OH)_2}$$

Salts of each of the anions have been isolated.[18,43] The lithium and sodium salts were obtained by the double decomposition of $K_4\left[W(CN)_4(OH)_4\right]$ with metal perchlorates. On interaction, the less soluble $KClO_4$ was precipitated out and filtered off and the alkali metal were crystallised by adding alkali and alcohol. The strontium and barium salts were prepared from acetates: $Sr(CH_3COO)_2 \cdot \frac{1}{2}H_2O$ and $Ba(CH_3COO)_2 \cdot H_2O$ by exchange reaction with the potassium salt. In this case, the relatively less soluble salts of alkaline earth metal hydroxocyanides precipitate out in the presence of alkali and the highly soluble potassium salts remain in the solution. The results of analyses correspond to the formulae: $Li_4\left[W(CN)_4(OH)_4\right] \cdot 10H_2O$, $Na_4\left[W(CN)_4(OH)_4\right] \cdot 10H_2O$, $Sr_2\left[W(CN)_4(OH)_4\right] \cdot 13H_2O$ and $Ba_2\left[W(CN)_4(OH)_4\right] \cdot 2H_2O$. Strontium salts of the tri- and di-substituted forms have the compositions

$Sr_3[W(CN)_4(OH)_3(H_2O)]\cdot 7H_2O$ and $Sr[W(CN)_4(OH)_2(H_2O)_2]\cdot 3H_2O$ respectively. A calcium salt, $Ca[W(CN)_4OH)_2(H_2O)]\cdot H_2O$ have also been reported. The hydroxotetracyanotungstate $K_4[W(CN)_4(OH)_4]$, have been found to be of strong reducing nature, which reduces Cd^{2+}, Cu^{2+}, Hg^{2+}, Tl^{3+}, Pb^{2+}, Sb^{3+}, Bi^{3+} and Pd^{2+} in alkaline solution to the corresponding metals. Ag^+ is first reduced to Ag in hot alkaline solution, partly as AgCN also. In natural solution, no reduction occurs, but all Ag^+ is precipitated as $Ag_4[W(CN)_4(OH)_4]\cdot Cu^{2+}$ reduces to Cu in alkaline solution at 25° Cu^{2+} reacts variously. At room temperature in alkaline solution a white $Cu_2(CN)_2$ precipitate with excess $K_4[W(CN)_4(OH)_4]$ at 40°, reduction to the metals occurs. On the reduction of copper ammine complex, the compounds:

$Cu(NH_3)[Cu_2(CN)_4(NH_3)_2]$, $Cu[Cu_4(CN)_6(NH_3)_2]$,

$K_2[Cu_2(CN)_4(NH_3)_2]$, $Cu\,Cu_2(CN)_4(NH_3)_2]$

have been obtained, the composition depending upon the relative concentrations, order of mixing and reaction kinetics. Potentiometric titrations of the hydroxocyanide with Cu_2^{2+}, Ag^+ and $Fe(CN)_6^{3-}$ in alkaline solution and with MnO_4^- in acid medium were successfully performed.

The formation and composition of Cr(III) and Fe(III) hydroxocyanotungstate(IV) was investigated amperometrically[6]

by titrating $CrCl_3$ or ferric alum with potassium hydroxocyanotungstate(IV) at applied potentials of 1.3 and 0.45v. Both direct and reverse titrations with varying concentrations indicated the formation of the 1:1 complex, $KM[W(CN)_4(OH)_4]$ (where M = Cr or Fe). The titration curves are so well defined that $K_4[W(CN)_4(OH)_4]$ can be used for the amperometric estimation of Cr^{3+} and Fe^{3+}. Both direct and reverse titrations between MSO_4 (where M=Co,Ni,Cu,Zn) and $K_4[W(CN)_4(OH)_4].\ 4H_2O$ gave a combining ratio of 1:1 suggesting the formation $K_2[MW(CN)_4(OH)_4]$.[6]

The hydrolysis constants for the tetra-, tri- and di-substituted hydroxocyanides have been reported (at 16°c) as 5.2×10^{-4}, 2.15×10^{-7} and 7.9×10^{-10}, and also their acid dissociation constants as 1.2×10^{-11}, 2.9×10^{-8} and 7.9×10^{-6} respectively.[18] The heat of combustion have also been determined.[44]

Collenberg[34] and later Baadsgard and Treadwell[43] measured the electrode potential for the change :

$$[W(CN)_8]^{3-} + e \rightleftharpoons [W(CN)_8]^{4-}$$

and gave values for the $E^{\circ}W^{V}/W^{IV}$ as + 0.57V (0° in the presence of KCl) and +0.475V (25°, u = 0), respectively. A value of $E^{\circ}\ W^{IV}/W^{V}$ = - 0.62V has been reported for a

saturated solution of $K_4[W(CN)_4(OH)_4]$ in alkaline medium.[40] Mikhalevich and Litvinchuk[41] made a detailed study of the redox properties of the tetrahydroxocyanotungstates(IV) and proposed the following redox mechanism:

$$\left[W^{IV}(CN)_4(OH)_4\right]^{4-} \rightleftharpoons \left[W^{V}(CN)_4(OH)_4\right]^{3-} + e \quad \text{(an equilibrium process), and}$$

$$\left[W^{V}(CN)_4(OH)_4\right]^{3-} + 4OH^- \longrightarrow WO_4^{2-} + 4CN^- + 4H_2O + e$$

(irreversible destruction of the complex). The redox potential depends strongly on pH and can be expressed by the equation:

$$E[ox]/[red] = E^0 + \frac{RT}{nF} \ln [ox.]/[red.] + \frac{m}{n}\frac{RT}{F}(7-pH)$$

which was further simplified to the equation:

$$E\ [ox]/\ [red.]\ = 0.07 + 0.029 \log [ox.]/[red.] + 0.116\ (7-pH)$$

by substituting the normal transition potential of the system in neutral medium, $E^0 = 0.07V$; the number of the hydrogen ions, $m = 4$; the number of electrons taking part in the process, $n = 2$; and $dE/d(pH) = 0.116$ V.

According to the above equation two electrons should be involved in the equilibrium process but the proposed

mechanism shows it to be a one-electron reversible oxidation. In a detailed study by Kabir-ud-Din et.al.[6] of the standard potential for the existing redox couple in 0.0-3M KOH at 298-323 K° is determined by potential mediator method by titration with $K_3Fe(CN)_6$. The slope of the standard potential vs.log [ox.] / [red.] is 0.03V confirming that the two electrons participate in the equilibrium process. The effect of KOH concentration on the E° value is similar to that of HCl on the $[Fe(CN)_6]^{4-}$ / $[Fe(CN)_6]^{3-}$ system. The oxidation potential increases with increase of ionic strength. On the basis of the detected E° values ΔG°, ΔH° and ΔS° are 32.4 Kcal/mole; 87.3Kcal/mole and 18.0Kcal/mole respectively at 298K°.

Basu and Basu[44] indicated the electronic absorption spectra of $K_4[W(OH)_4(CN)_4]$ have a geometry different from dodecahedral, at least in aqueous solution.

Litvinchuk et.al[45] reported the absorption spectra for $K_4[W(OH)_4(CN)_4]$, maximum absorption occurs at 540 nm while minimum at 380 nm. They have also detected the optical activation energy for the crystals of the absorption band edge.

The recent crystallographic work has established that the hydroxocyanides are best formulated as six coordinate

oxocyanides instead of previous eight coordinate formulations. The compound $K_4[WO_2(CN)_4] \cdot 6H_2O$ is shown to have two oxygen atoms trans to each other.[38]

The above account clearly shows that little work has so far been done as regards the physico-chemical properties of alkali oxocyanogen compounds of molybdenum and tungsten. No doubt Pool and Neumann[37] have made a valuable contribution in determining the values of acid dissociation constants, but the problem related with the influence of ionic strength, temperature etc. is not clear. Mikhalevich[12] has recently studied the interaction of ammine complexes of Ag and of Cu with complex cyanides.

The work described in this thesis deals with some physico-chemical aspects of tripotassium oxohydroxotetracyanomolybdate(IV) (referred to herein as TCM) and tetrapotassium dioxotetracyanotungstate(IV) (referred to herein as TCT) which need a more systematic approach and further elucidation. Certain ammine complexes of both TCM and TCT have also been investigated employing physical methods.

The distribution of various aspects studied is as follows:

1. Polarographic studies in aqueous medium.
2. Determination of acid dissociation constants.
3. Composition of Cu, Ag, Ni and Co ammine complexes of TCM and Ni and Co ammine complexes of TCT.

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C H A P T E R - I:

Polarographic Studies of Tripotassium oxo-hydroxo-tetracyanomolybdate(IV) and Tetrapotassium Dioxo-tetracyanotungstate(IV) in aqueous medium.

Although, some work has been done on the polarographic behaviour of octacyanides of molybdenum and tungsten[1,2] the existing chemical literature finds no mention of the polarographic studies of any of the oxocyanides of molybdenum and tungsten.

Both the ions, oxohydroxocyanomolybdate(IV), $[MoO(OH)(CN)_4]^{3-}$ and dioxotetracyanotungstate(IV), $[WO_2(CN)_4]^{4-}$ produce two anodic waves in 0.1M KNO_3 aqueous solution. It has been further found by log plot analysis that the first step oxidation is reversible and the second one is irreversible in case of the former ion while the oxidation steps are of reverse order in the case of latter ion. The apparent kinetic parameters for the irreversible oxidation processes have been evaluated by employing Koutecky's theoretical treatment[3] as extended by Meites and Israel.[4] The treatment is detailed as under:

In its simplest form, the mechanism responsible for totally irreversible wave may be described by the equation

$$O + ne \longrightarrow R \qquad (1)$$

The cathodic current i_c (in microamperes) that results from the reduction of O(oxidised species) at any potential is described by the equation.

$$i_c = nFAC^{o}ok' \exp\left[\alpha - nF(E-E')/RT\right] \qquad (2)$$

where F is the number of coulombs perfaraday, A is the area of the electrode (in $cm.^2$), Co^o is the concentration of O at the surface of the electrode (in millimoles/1000 $cm.^3$), α is the transfer coefficient, R is the gas constant (in volt-coulombs per degree), and T is the absolute temperature; k' is the value of the rate constant for the electrode reaction when the electrode potential E is equal to the reference value E'. Because the reaction is heterogeneous (the electron transfer occurs across the phase boundary between mercury and solution), k' is expressed in cm./sec. rather than in $sec.^{-1}$ as the rate constant of a homogeneous first-order reaction would be.

Two choices of the reference potential E' are of interest. One is the formal potential $E^{\grave{o}}$ of the O-R couple in the solution under consideration. The value of k' at this potential is denoted by the symbol $k_{s,h}$, so that eq. (2) becomes

$$i_c = nFAC^o ok_{s,h} \exp\left[-\alpha nF(E - E^{o'})/RT \right] \cdots \quad (3)$$

For couples whose formal potentials are unknown or even (as is the case for many totally irreversible couples) unmeasurable, a more convenient though sometimes less readily interpretable choice is O v. vs. N.H.E. (-0.2412 v.vs.S.C.E.).

Here the value of k' is denoted by the symbol $k^{o}_{f,h}$, so that eq. (2) becomes

$$i_c = nFAC^{o}ok^{o}_{f,h} \exp\left[-\alpha nF(E + 0.2412)/RT \right] \ldots\ (4)$$

where E is referred to the S.C.E.

Similar equations,

$$i_a = nFAC^{o}_{R}k_{s,h} \exp\left[(1 - \alpha)\, nF(E-E^{o'})/RT \right] \ldots\ (5)$$

and

$$i_a = nFAC^{o}_{R}k^{o}_{b,h} \exp\left[(1-\alpha)\, nF(E+ 0.2412)/RT\right] \ldots\ (6)$$

in both of which it is the numerical or absolute value of n that appears in the exponent, may be written for the anodic current resulting from the oxidation of R. The value of $k_{s,h}$ appearing in eq. (5), as is easily shown on recognizing that if $C_R^{o} = Co^{o}$ the net current must be zero at the formal potential, which can be the case only if i_c and i_a numerically equal though opposite in sign. Hence $k_{s,h}$ is a fundamental parameter characteristic of the couple. On the other hand, the value of $k^{o}_{b,h}$ (the rate constant for the backward or oxidation process at E = 0 v. vs. N.H.E.) may differ from that of $k^{o}_{f,h}$ by many orders of magnitude.

Koutecky gave values for the function F(X) where X and subsidiary variable λ are defined by the following equation

for irreversible cathodic wave:

$$\lambda = (7/12)^{\frac{1}{2}} X = k_{f,h} \left(\frac{t}{D}\right)^{\frac{1}{2}} \quad \ldots\ldots \quad (7)$$

In this equation t is the drop-time, D is the diffusion coeffecient of the electroactive substance and $k_{f,h}$ is the potential-dependent heterogeneous rate constant. Neglecting changes in the structure of the electrical double layer[5] $k_{f,h}$ may be defined as (at 25°c):

$$k_{f,h} = k^{\circ}_{f,h} \exp\left[-\alpha nF\ (E + 0.2412)/RT\right] \ldots\ldots \quad (8)$$

For a totally irreversible process it is given that

$$i/i_d = F(X) \quad \ldots\ldots \quad (9)$$

Meits and Israel found that log X varies linearly with $\log\left[F(X)/1-F(X)\right]$ according to the following equation:

$$\log X = -0.0130 + 0.9163 \log\left[F(X)/1-F(X)\right] \ldots \quad (10)$$

The value of log X can be obtained with the help of equation (7) and (8):

$$\log X = \log\left[(12/7)^{\frac{1}{2}} k_{f,h} (t/D)^{\frac{1}{2}}\right] = \log(12/7)^{\frac{1}{2}} + \log k_{f,h} (t/D)^{\frac{1}{2}}$$

$$= 0.1170 + \log k^{\circ}_{f,h} (t/D)^{\frac{1}{2}} + \left[-\alpha nF(E+0.2412)/2.303\ RT\right] \ldots\ldots (11)$$

Putting this value of log X in equation (10) we obtain:

$$0.1170 + \log k^{\circ}_{f,h} (t/D)^{\frac{1}{2}} + \left[-\alpha nF(E + 0.2412/2.303\ RT\right]$$

$$= -0.0130 + 0.9163 \log\left[F(X)/1-F(X)\right] = -0.0130 + 0.9163 \log(1/i_d - 1)$$

$$\text{or } \alpha nF(E + 0.2412)/2.303\ RT = 0.1300 + \log k^{\circ}_{f,h}(t/D)^{\frac{1}{6}} - 0.9163 \log (1/i_d - 1)$$

$$\text{or } \alpha n(E + 0.2412)/0.0591 = 0.1300 + \log k^{\circ}_{f,h}(t/D)^{\frac{1}{6}} - 0.9163 \log (1/i_d - 1) \text{ (at } 25^{\circ}\text{c)}$$

$$\text{or } E + 0.2412 = \frac{0.13 \times 0.0591}{\alpha n} + \frac{0.0591}{\alpha n} \log \left[k^{\circ}_{f,h}(t/D)^{\frac{1}{6}} \right] - \frac{0.9163 \times 0.0591}{\alpha n} \log (1/i_d - 1) .$$

$$= \frac{0.0591}{\alpha n} \left[0.130 + \log k^{\circ}_{f,h}(t/D)^{\frac{1}{6}} \right] - \frac{0.0542}{\alpha n} \log (1/i_d - 1)$$

$$E_{d.e.} + 0.2412 = \frac{0.0591}{\alpha n} \log 1.349\, k^{\circ}_{f,h}(t/D)^{\frac{1}{6}} - \frac{0.0542}{\alpha n} \log (1/i_d - 1) \qquad \ldots\ldots \qquad (12)$$

As drop-time also varies with applied potential according to the equation

$$\log t = k_1 + k_2 E_{d.e.}$$

it is preferable to use equation(12) in the following form

$$E_{d.e.} + 0.2412 = \frac{0.0591}{\alpha n} \log 1.349\, k^{\circ}_{f,h}/D^{\frac{1}{6}} + \frac{0.0591}{\alpha n} \log t^{\frac{1}{6}} - \frac{0.0542}{\alpha n} \log (1/i_d - 1) = \frac{0.0591}{\alpha n} \log 1.349\, k^{\circ}_{f,h}/D^{\frac{1}{6}} + \frac{0.0295}{\alpha n} \log t - \frac{0.0542}{\alpha n} \log (1/i_d - 1)$$

$$E_{d.e.} + 0.2412 = \frac{0.0591}{\alpha n} \log 1.349\, k^{\circ}_{f,h}/D^{\frac{1}{6}} - \frac{0.0542}{\alpha n} \left[\log 1/i_d - 1 - 0.546 \log t \right] \qquad \ldots\ldots \qquad (13)$$

which may be written as

$$E_{d.e.} = E_{\frac{1}{2}}^{o} - \frac{0.0542}{\alpha n} \log (i/i_d - i) \quad \ldots\ldots \quad (14)$$

$$\text{with } E_{\frac{1}{2}}^{o} = -0.2412 + \frac{0.0591}{\alpha n} \log \frac{1.349 k_{f,h}^{o} t^{\frac{1}{6}}}{D^{\frac{1}{2}}} \quad \ldots\ldots \quad (15)$$

In these equations both $E_{d.e.}$ and $E_{\frac{1}{2}}$ are referred to the S.C.E. . In equation(14) currents are those at the ends of the drop-lives and not the average currents, as the kinetic parameters are more accurately reproduced by measuring the maximum currents.

To obtain identical equations for anodic waves, αn is replaced by $-(1-\alpha)n = -\beta n$ where $\alpha + \beta = 1$ and $k_{f,h}^{o}$ by $k_{b,h}^{o}$, then (at 25^{o}) :

$$E_{d.e.} = E_{\frac{1}{2}}^{o} + \frac{0.0541}{\beta n} \left[\log(i_d - i/i) - 0.546 \log t\right] \quad \ldots\ldots \quad (16)$$

$$\text{Where } E_{\frac{1}{2}}^{o} = -0.2412 - \frac{0.0591}{\beta n} \log \frac{1.349 k_{b,h}^{o}}{D^{\frac{1}{2}}} \quad \ldots\ldots \quad (17)$$

Polarographic studies of TCM and TCT ions have been performed for evaluating the kinetic parameters and for gaining information about their electrochemical behaviours at the dropping mercury electrode.

EXPERIMENTAL

Reagents:

Tripotassium oxohydroxotetracyanomolybdate(IV)dihydrate, $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$(TCM): This blue cyanide was precipitated by treating an aqueous solution of the dioxo-cyanide, $K_4[MoO_2(CN)_4]$, with ethyl alcohol. The method recommended by Jakob and Turkiewicz[6] and later modified by Jakob and Jakob[7] for preparation of the red cyanide was followed.

Pure molybdenum(VI) oxide, MoO_3, dissolved in hot concentrated HCl (1.5 ml./g.MoO_3) was reduced with hydrazine sulphate. The resulting red-brown solution of molybdenyl hydroxide was filtered and diluted to a large volume with water. It was then precipitated with a small excess of ammonia, washed and filtred off. Molybdenyl hydroxide, $MoO(OH)_3$, thus obtained, was placed in a flask. To this a concentrated solution of 2.5 moles of potassium cyanide per mole of molybdenum was added and the contents were heated over a water-bath with constant stirring. Then 0.25 mole of solid potassium hydroxide was also added. Evaporation of water under reduced pressure at 70°c was accomplished until a blue precipitate appeared. Solid KOH was then added slowly to this solution which, on cooling, separated out the

red-brown crystals of $K_4[MoO_2(CN)_4]$. These crystals were collected on a Buchner funnel and washed with alcohol.

The reaction which takes place during the synthesis may be represented by the equation:

$$2MoO(OH)_3 + 4KCN + KOH = K_3[MoO(OH)(CN)_4] + K_2MoO_4 + 3H_2O$$

By the action of excess of alkali, the less soluble tetra-potassium salt separates out:

$$K_3[MoO(OH)(CN)_4] + KOH = K_4[MoO_2(CN)_4] + H_2O$$

The tetra potassium salt was dissolved in distilled water to give the soluble TCM which was then fractionally precipitated with ethanol. The mother liquor was alkaline indicating that by the conversion of the red into the blue cyanide, KOH was released. The blue solid was redissolved in the smallest possible quantity of water and reprecipitated with alcohol; these operations were repeated several times until the mother liquor was no more alkaline. The blue precipitate was collected on a Buchner funnel, washed with alcohol, ether and kept over $CaCl_2$ in a vacuum desiccator.

Anal. Calcd for $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$: C, 12.43; N, 14.51; H, 1.30. Found: C, 12.26; H, 0.73; N, 14.51.

Tetra Potassium dioxotetracyanotungstate(IV) hexa hydrate, $K_4[WO_2(CN)_4].6H_2O$(TCT): This complex oxocyanide was prepared following directions of Mikhalevich and Litvinchuk.[8] Fifty grams of ammonium paratungstate was added to 500 ml. of water at a temperature of 80° and then 50 grams of oxalic acid and 30 grams of ammonium oxalate were slowly added with stirring. A transparent solution was obtained which was then electrically reduced at a current density of 0.05 amp./cm^2 by using a perforated platinum gauze cathode. The experiment was conducted while heating up to 80-90° for 6 to 8 hours. The colour changes during the reduction were from colourless to dark blue to greenish-yellow to reddish-brown. After cooling, the cathode solution was filtered and neutralized with a low percent ammonia solution until the light-brown amorphous precipitate of tungstyl hydroxide, $WO(OH)_3$, was fully formed. This was filtered out, washed with cold water and transferred into a round bottomed flask. A solution of 23 grams KCN and 20 grams of KOH in 100 ml. of water was added to it in portions in the course of 15 minutes. The contents of the vessel were simultaneously stirred and heated to 60° on a water bath. Dissolution of the brown precipitate gave a purple-violet solution. After cooling, the solution was filtered. The solid oxocyanide separated by

slow addition of 60 grams of solid KOH to 200 ml. of the solution. Yellowish-brown crystals of the oxocyanide separated out. For further purification, the compound was dissolved in the smallest possible quantity of water and reprecipitated by the addition of solid alkali. The crystals were collected on a Buchner funnel, washed with alcohol, ether and kept over $CaCl_2$ in a vacuum desiccator.

Anal.Calcd. for $K_4[WO_2(CN)_4]\cdot 6H_2O$: C,8.21; H,2.07; N,9.57. Found: C, 9.17; H, 2.04; N, 10.20.

The reactions during the synthesis are similar to those in the preparation of oxohydroxomolybdocyanide:

$$2WO(OH)_3 + 4KCN + KOH = K_3[WO(OH)(CN)_4] + K_2WO_4 + 3H_2O$$

$$K_3[WO(OH)(CN)_4] + KOH = K_4[WO_2(CN)_4] + H_2O$$

The solution of the compound was made in conductivity water and was standardised by titrating potentiometrically against potassium hexacyanoferrate[9](III).

Potassium hexacyanoferrate(III) solution: Potassium ferricyanide solution was prepared by dissolving recrystallised and air-dried AnalaR-grade(B.D.H.) product in conductivity water. The strength was checked by titrating iodometrically using standard $Na_2S_2O_3$ solution.[10]

All other materials used were either of AnalaR-grade (B.D.H.) or Merck's reagent-grade chemicals.

Apparatus: Pye Precision Vernier Potentiometer (Cat.No.7568) in conjunction with a ballistic galvanometer and lamp and scale arrangement was employed for potential measurements. A bright platinum electrode was used as an indicator and a saturated calomel electrode as the reference electrode.

Polarographic studies were carried out using a manual Toshniwal polarograph (Type CLO 2A) in conjunction with Toshniwal galvanometer (Cat.No.PL 64.01) and Fischer Elecdropode. The electrodes used were saturated calomel and dropping mercury. A side tube from the reference electrode with porous end-plate, filled with KNO_3(satd)-agar, was used to connect the two halves of the cell. The cell and the reference electrode were kept in a water thermostat. Double distilled mercury was used in the DME. All the measurements were made in a darkened room. Prior to observations, each solution was deoxygenated by a stream of nitrogen which had been passed successively through chromous chloride and alkaline pyrogallol solutions. Cylinder nitrogen supplied by Indian Oxygen Ltd., was used.

The effect of variation of depolarizer concentration, drop-time and temperature was studied to establish characteristics of the waves.

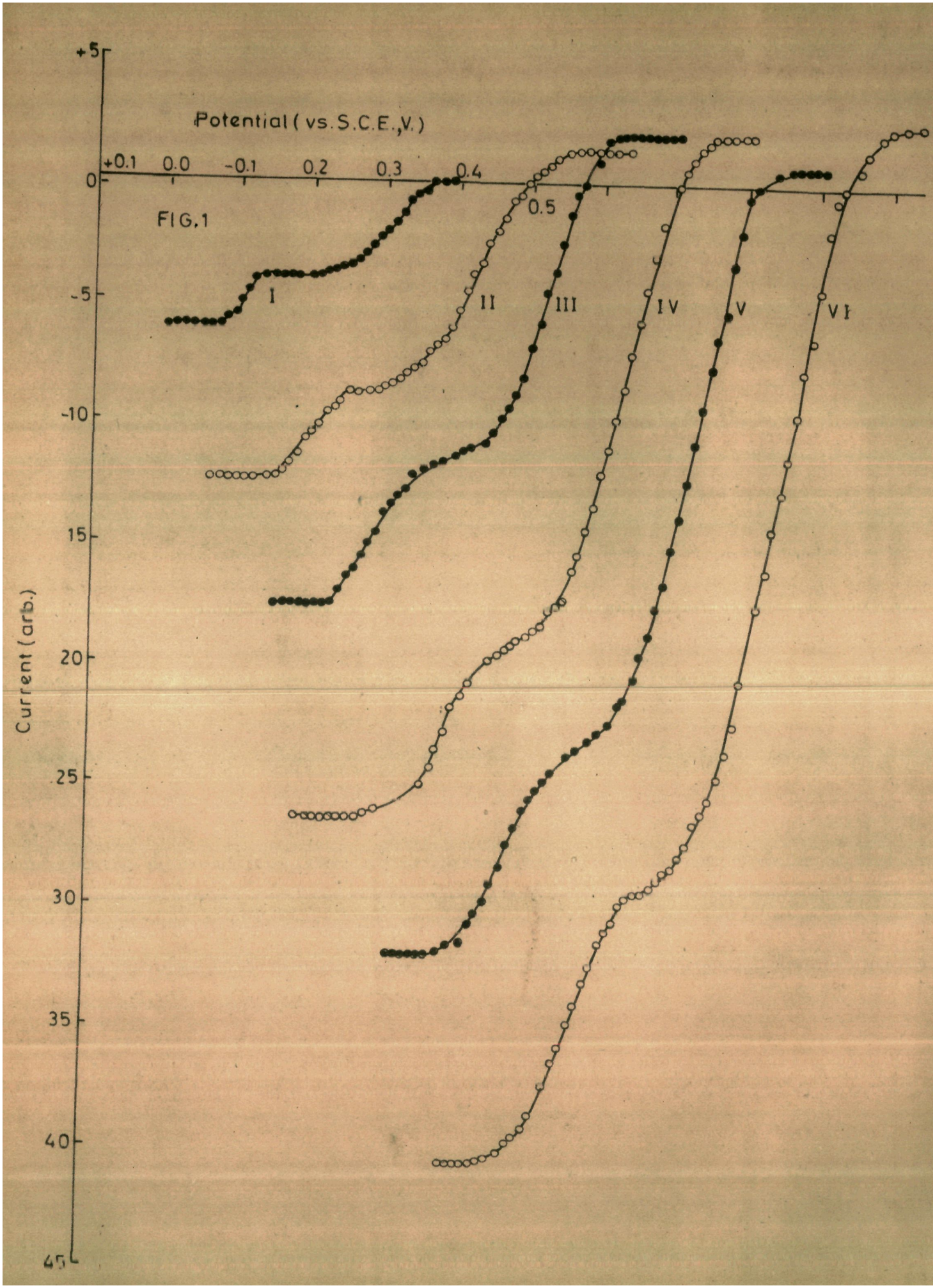

+5
Potential (vs. S.C.E., V.)
+0.1
0.0
-0.1
0.2
0.3
0.4
0.5
0
-5
-10
15
20
25
30
35
40
45
Current (arb.)
I
II
III
IV
V
VI

FIG. 1

(A) OXOHYDROXOCYANOMOLYBDATE(IV) ION

Effect of depolarizer concentration:

Polarograms of the TCM ranging from 0.5 mM to 3.0 mM were taken at 25°c in the presence of 0.01% gelatin and 0.1M KNO_3 solutions. Two well defined anodic waves were obtained. The following table record the observations:

T A B L E - 1.

[t = 4.62 sec., m = 1.778 mg./sec., h = 81.25 cm.(open circuit)]

Potential (vs SCE,V.)	Current (arbitrary)					
	Concn.of TCM(mM)					
	0.5	1.0	1.5	2.0	2.5	3.0
+0.10	-	-	-	-	-	-40.5
0.09	-	-	-	-	-	40.5
0.08	-	-	-	-	-32.0	40.5
0.07	-	-	-	-26.25	32.0	40.5
0.06	-	-	-	26.25	32.0	40.5
0.05	-	-	-17.5	26.25	32.0	40.25
0.04	-	-12.25	17.5	26.25	32.0	40.25
0.03	-	12.25	17.5	26.0	32.0	40.0
0.02	-	12.25	17.5	26.0	31.5	40.0
0.01	-	12.25	17.5	25.75	31.5	39.5

(Contd.)

T A B L E -1.(Contd.)

0.0	-6.0	12.25	17.5	25.75	-	39.25
-0.01	6.0	12.25	17.5	-	-	39.0
0.02	6.0	12.25	17.5	-	31.5	38.5
0.03	6.0	12.25	17.5	-	30.75	37.25
0.04	6.0	12.25	17.0	-	30.25	37.25
0.05	6.0	12.25	16.25	-	29.75	36.25
0.06	6.0	12.0	16.0	25.0	29.0	35.75
0.07	6.0	11.75	15.5	24.25	28.25	34.75
0.08	5.75	11.25	15.0	23.5	27.25	34.0
0.09	5.5	10.75	14.5	22.75	26.75	33.0
0.10	5.0	10.5	13.75	21.75	26.0	32.5
0.11	4.5	10.0	13.25	21.25	25.5	31.5
0.12	4.0	9.5	13.0	20.75	25.25	31.0
0.13	4.0	9.25	12.75	20.75	24.75	30.5
0.14	4.0	9.0	12.0	19.75	24.25	29.75
0.15	4.0	8.75	12.0	19.75	23.75	29.5
0.16	4.0	8.75	11.75	19.5	23.75	29.25
0.17	4.0	8.75	11.75	19.25	23.5	29.25
0.18	4.0	8.75	11.5	19.0	23.0	29.0
0.19	4.0	8.75	11.5	19.0	23.0	28.75
0.20	4.0	8.5	11.25	18.75	22.75	28.25
0.21	4.0	8.25	11.0	18.5	22.75	28.25

(Contd.)

T A B L E -1(Contd.)

0.22	3.75	8.25	11.0	18.25	22.25	27.75
0.23	3.75	8.0	10.75	17.75	21.5	27.25
0.24	3.5	7.75	10.75	17.5	21.25	26.25
0.25	3.5	7.5	10.25	17.25	20.5	26.0
0.26	3.25	7.0	9.75	16.0	19.5	25.25
0.27	3.0	6.75	9.25	15.25	18.75	24.5
0.28	2.75	6.5	8.75	14.5	17.5	23.5
0.29	2.25	6.0	8.0	13.25	16.5	22.25
0.30	2.0	5.25	6.75	12.0	15.0	20.5
0.31	1.75	4.5	5.75	11.0	13.75	-
0.32	1.25	3.75	4.5	9.75	12.25	17.5
0.33	0.75	3.25	3.75	8.5	10.75	16.0
0.34	0.50	2.5	2.5	7.0	9.25	14.25
0.35	0.25	2.0	1.25	5.75	7.75	12.75
0.36	0.0	1.5	0.5	4.25	6.25	11.25
0.37	0.0	0.75	0.0	3.0	5.25	9.5
0.38	0.0	0.5	0.0	1.75	3.25	7.75
0.39	0.0	0.0	+1.0	0.0	2.0	6.25
0.40	0.0	+0.25	1.75	0.0	0.5	4.25
0.41	0.0	0.5	1.75	+0.5	0.0	2.0
0.42	0.0	0.75	2.0	1.0	0.0	0.5
0.43	0.0	1.0	2.0	1.5	0.0	0.0

(Contd.)

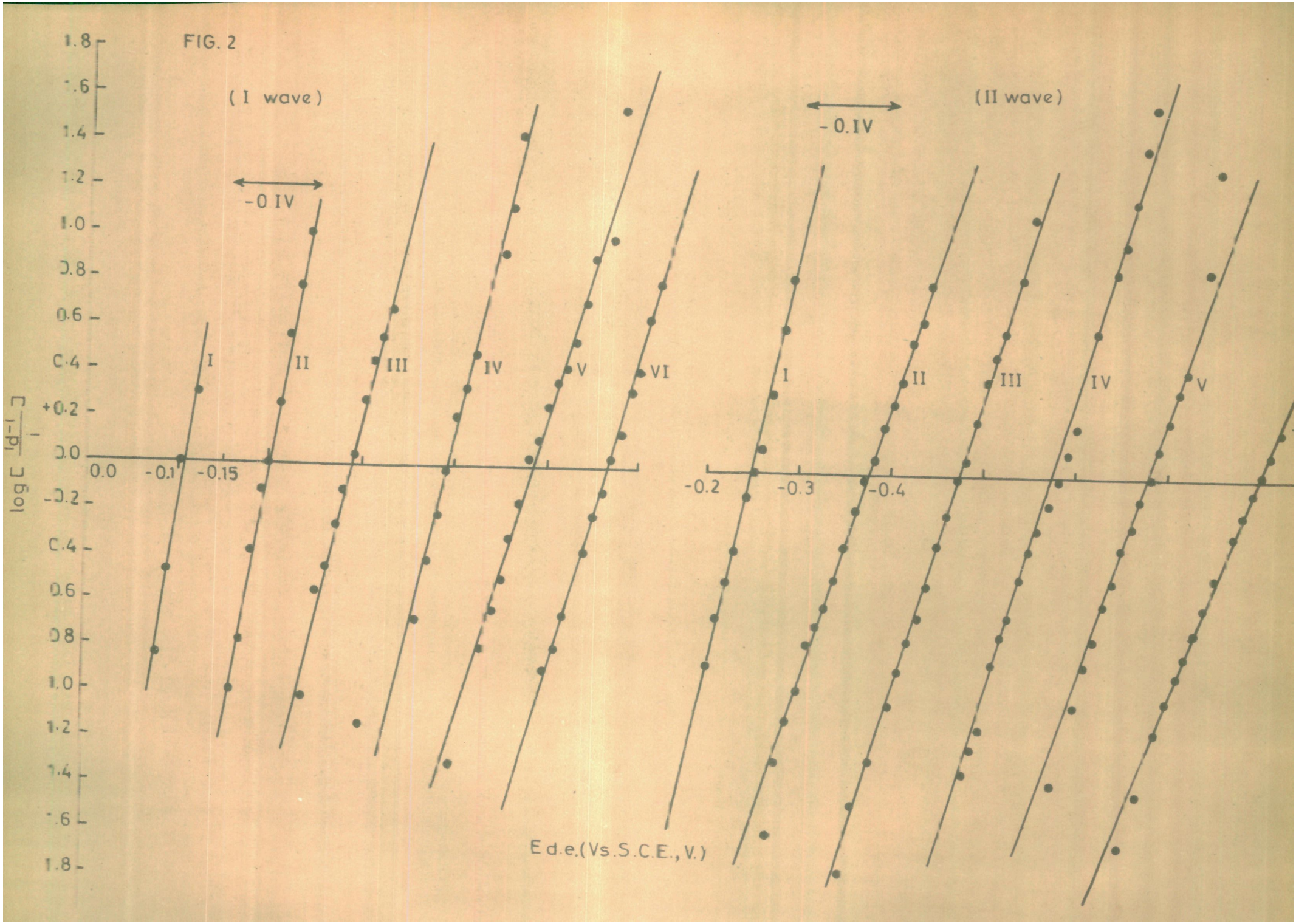


FIG. 2
(I wave)
-0 IV
(II wave)
- 0.1V
I
II
III
IV
V
VI
0.0
-0.1
-0.15
-0.2
-0.3
-0.4
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
+0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
log [i-pl]/[i]
Ed.e.(Vs.S.C.E., V.)

T A B L E -1.(Contd.)

0.44	0.0	1.0	2.25	1.75	+0.5	0.0
0.45	0.0	1.25	2.25	2.0	0.75	+0.75
0.46	-	1.25	2.0	2.0	0.75	1.25
0.47	-	1.25	2.0	2.0	0.75	1.5
0.48	-	1.25	2.0	2.0	0.75	2.0
0.49	-	1.25	2.0	2.0	0.75	2.25
0.50	-	1.25	2.25	2.25	0.75	2.5
0.51	-	1.25	2.25	2.25	0.75	2.5
0.52	-	1.25	2.25	2.25	0.75	2.5
0.53	-	1.25	2.25	2.25	0.75	2.5
0.54	-	1.25	2.25	2.25	0.75	2.5
0.55	-	1.25	2.25	2.25	0.75	2.5
Fig.1	Curve(I)	Curve(II)	Curve(III)	Curve(IV)	Curve(V)	Curve(VI))

The reversibility of the electrode reaction was tested by plotting $\log(i_d - i/i)$ versus $E_{d.e.}$. The plots Fig.(2) show that the first oxidation step is reversible (as the slope was always found to be in the range of 0.059 - in good agreement with the theoretical value of 0.05915 at 25°c) corresponding to the loss of one electron. The second step oxidation is irreversible as the slope was in the range of 0.09.

FIG. 3

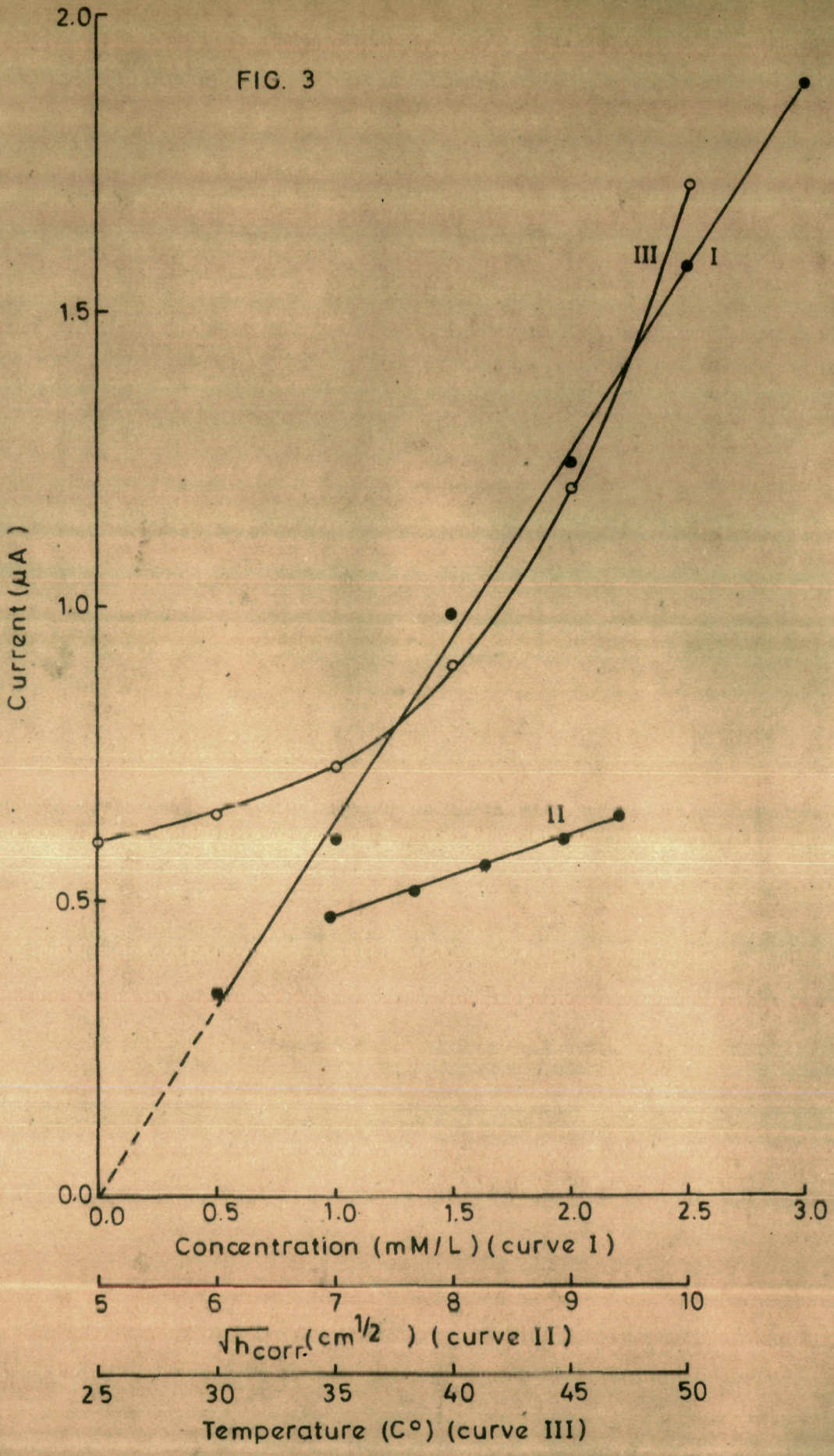
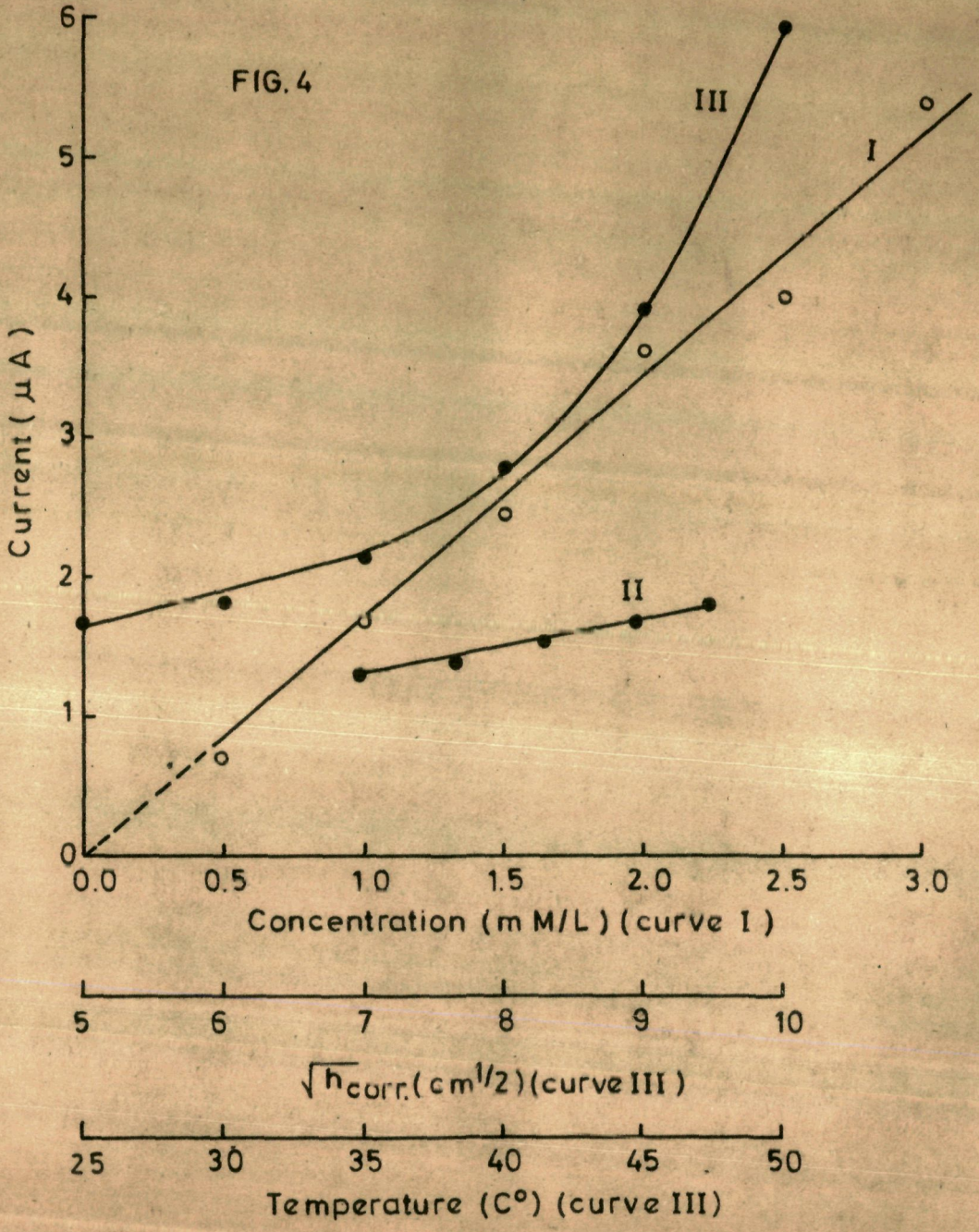

2.0
1.5
1.0
0.5
0.0
Current (μA)
III
I
II
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Concentration (mM/L) (curve I)
5
6
7
8
9
10
√h corr. (cm^1/2) (curve II)
25
30
35
40
45
50
Temperature (C°) (curve III)

FIG. 4


Current (μA)
0
1
2
3
4
5
6
III
I
II
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Concentration (m M/L) (curve I)
5
6
7
8
9
10
√h corr. (cm^1/2) (curve III)
25
30
35
40
45
50
Temperature (C°) (curve III)

The following table shows the test for the linearity of the wave heights with depolarizer concentration.

TABLE-2.

Concn. of TCM (mM)	i_d (μA)	i_d/C	$I = i_d/C\ m^{\frac{2}{3}}t^{1/6}$	$-E_{\frac{1}{2}}$ (Vs. SCE, V)
		For First Wave		
0.5	0.342	0.684	0.361	0.10
1.0	0.598	0.598	0.316	0.095
1.5	0.983	0.655	0.346	0.09
2.0	1.239	0.620	0.327	0.09
2.5	1.572	0.629	0.332	0.09
3.0	1.881	0.627	0.331	-
Means		0.635_5	0.335_5	
		For Second Wave		
0.5	0.684	1.368	0.722	0.30
1.0	1.667	1.667	0.880	0.33
1.5	2.437	1.624	0.857	0.335
2.0	3.591	1.795	0.948	0.33
2.5	3.976	1.590	0.840	0.33
3.0	5.386	1.795	0.948	-
Means	-	1.639_8	0.865_8	

The above table shows that the values of i_d/C and I are constant within the experimental error. The relation between wave heights and depolarizer concentration is shown in figures 3 and 4 (curves I), which shows a linear relationship

+5
0
-5
10
15
Current (arb.)
0.0
-0.1
0.2
0.3
0.4
0.5
Potential (vs. S.C.E, V.)
I
II
III
IV
V

FIG. 5

between the wave heights and concentration for both the waves passing through the origin. Thus TCM can be estimated quantitatively in the range 0.5-3.0mM taking into consideration either of the two waves.

Effect of drop-time:

A series of polarograms of 1.0 mM TCM were drawn at different heights of mercury column at 25°. The following tables record the observations:

T A B L E -3.

Potential Vs.SCE,V.)	Current (arbitrary)				
	Heights (cm.)				
	50.0	60.0	70.0	81.25	90.0
+0.05	-	-	-12.0	-	-12.75
0.04	-	-	12.0	-12.25	12.75
0.03	-	-	12.0	12.25	12.75
0.02	-	-	12.0	12.25	12.75
0.01	-	-11.5	12.0	12.25	12.75
0.0	-10.5	11.5	12.0	12.25	12.75
-0.01	10.5	11.5	12.0	12.25	12.75
0.02	10.5	11.5	12.0	12.25	12.5
0.03	10.5	11.5	12.0	12.25	12.5

(Contd.)

T A B L E -3 (Contd.)

0.04	10.5	11.5	11.75	12.25	12.25
0.05	10.25	11.25	11.5	12.25	12.0
0.06	10.0	11.25	11.25	12.0	11.75
0.07	9.75	11.0	11.0	11.75	11.5
0.08	9.5	10.75	10.75	10.25	11.25
0.09	9.0	10.25	10.25	10.75	10.75
0.10	8.75	10.0	10.0	10.5	10.25
0.11	8.5	9.5	9.75	10.0	10.0
0.12	8.0	9.25	9.25	9.5	9.75
0.13	8.0	9.0	9.0	9.25	9.5
0.14	7.75	8.75	8.75	9.0	9.25
0.15	7.75	8.75	8.75	8.75	9.0
0.16	7.75	8.5	8.5	8.75	9.0
0.17	7.75	8.5	8.5	8.75	9.0
0.18	7.75	8.5	8.5	8.75	9.0
0.19	7.75	8.25	8.25	8.75	8.75
0.20	7.5	8.25	8.25	8.5	8.5
0.21	7.5	8.0	8.0	8.25	8.25
0.22	7.5	8.0	8.0	8.25	8.25
0.23	7.5	8.0	7.75	8.0	8.0
0.24	7.25	7.75	7.5	7.75	8.0
0.25	7.25	7.5	7.25	7.5	7.5

(Contd.)

T A B L E -3(Contd)

0.26	7.0	7.25	7.0	7.0	7.0
0.27	6.75	6.75	6.75	6.75	6.75
0.28	6.5	6.5	6.25	6.5	6.5
0.29	6.0	6.0	6.0	6.0	6.0
0.30	5.5	5.5	5.75	6.25	5.5
0.31	5.0	5.0	5.0	4.5	4.5
0.32	4.75	4.75	4.5	3.75	3.75
0.33	4.25	4.25	4.0	3.25	3.25
0.34	3.75	3.75	3.25	2.5	2.5
0.35	3.25	3.25	2.5	2.0	2.0
0.36	2.75	3.0	2.0	1.5	1.5
0.37	2.5	2.5	1.5	0.75	0.75
0.38	2.25	2.25	0.75	0.5	0.5
0.39	1.75	2.0	0.25	0.0	0.0
0.40	1.5	1.5	0.0	+0.25	+0.25
0.41	1.0	1.25	+0.25	0.5	0.5
0.42	0.75	0.75	0.25	0.75	0.75
0.43	0.5	0.5	0.5	1.0	1.0
0.44	0.25	0.25	0.5	1.0	1.25
0.45	0.25	0.0	0.5	1.25	1.25
0.46	0.0	0.0	0.5	1.25	1.5
0.47	0.0	0.0	0.5	1.25	1.5
0.48	0.0	0.0	0.5	1.25	1.5
0.49	0.0	0.0	0.5	1.25	1.5
0.50	0.0	0.0	0.5	1.25	1.5
Fig.5	Curve(I)	Curve(II)	Curve(III)	Curve(IV)	Curve(V)

TABLE-4.

Effect of mercury pressure:

$\left[MoO(OH)(CN)_4\right]^{3-}$ = 1.0 mM, KNO_3 = 0.1M, gelatin = 0.01% (25°c).

h_{Hg} (cm.)	m (mg./sec.)	t (sec.)	mt (mg.)	$h_{corr.}$ (cm.)	$h^{\frac{1}{2}}_{corr.}$ ($cm^{\frac{1}{2}}$.)	$100m/h_{corr.}$	i_d' (μA)	i_d'' (μA)	$i_d'/h^{\frac{1}{2}}_{corr.}$	$i_d''/h^{\frac{1}{2}}_{corr.}$
50.0	1.988	4.15	8.290	88.47	9.406	2.249	0.641	1.795	0.068	0.190
60.0	1.778	4.62	8.215	79.72	8.930	2.208	0.598	1.667	0.067	0.187
70.0	1.516	5.48	8.308	68.47	8.273	2.214	0.556	1.539	0.067	0.186
81.25	1.301	6.46	8.403	58.47	7.673	2.230	0.513	1.368	0.067	0.179
90.0	1.041	8.23	8.569	48.47	7.033	2.105	0.470	1.282	0.067	0.182
Means	-	-	8.357_0	-	-	2.201_2	-	-	0.067_2	0.184_8

Back pressure = $3.1/(mt)^{\frac{1}{3}} = 3.1/(8.357)^{\frac{1}{3}} = 1.528 \approx 1.53$

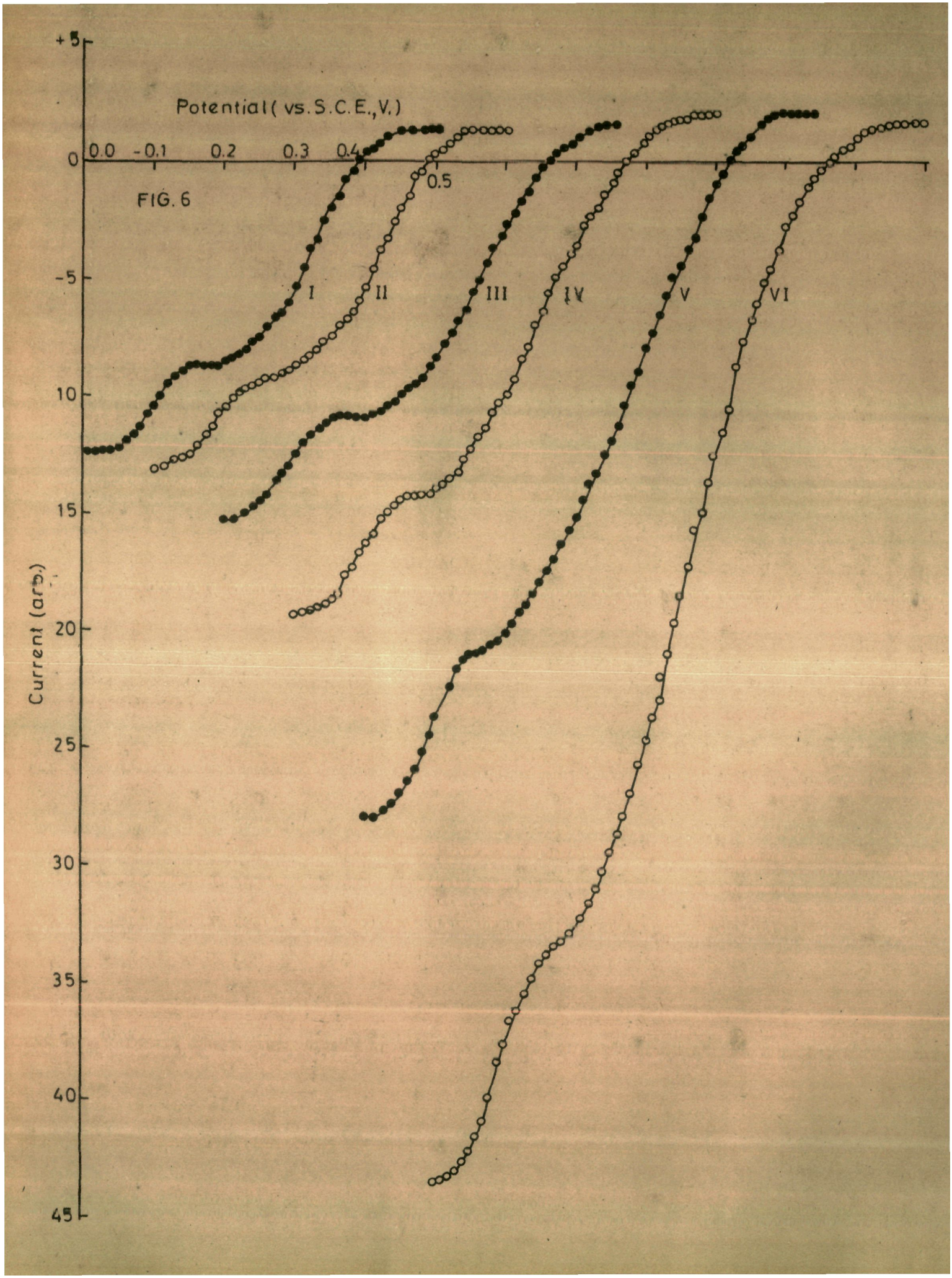

+5
0
-5
10
15
20
25
30
35
40
45
Current (arb.)
Potential (vs. S.C.E., V.)
0.0
-0.1
0.2
0.3
0.4
0.5
I
II
III
IV
V
VI

FIG. 6

Figures 3 and 4 (curves II) show that i_d vs. $h^{\frac{1}{2}}_{corr.}$ passing through origin, thereby proving that both the oxidation processes are diffusion controlled.

Effect of temperature:

Polarograms of 1.0mM TCM were taken in the temperature range of 25 to 50°c. The observations are recorded in table no.5 and i_d's and temperature coefficients are given in table no.6.

T A B L E -5.

[t = 4.62 sec., m = 1.778 mg./sec., h= 81.25 cm.]
(open circuit)

Potential (vs.SCE,V)	Current(arbitrary) Temperatures(°C)					
	25	30	35	40	45	50
+0.05	-	-13.0	-15.25	-19.25	-28.0	-43.5
0.04	-12.25	13.0	15.25	19.25	28.0	43.5
0.03	12.25	13.0	15.25	19.25	28.0	43.5
0.02	12.25	13.0	15.25	19.25	28.0	43.5
0.01	12.25	13.0	15.25	19.25	28.0	43.5
0.0	12.25	13.0	15.25	19.25	28.0	43.5
-0.01	12.25	13.0	15.25	19.25	28.0	43.5

(Contd.)

T A B L E -5(Contd.)

0.02	12.25	13.0	15.0	19.25	27.75	43.25
0.03	12.25	12.75	15.0	19.0	27.75	43.0
0.04	12.25	12.75	14.75	19.0	27.5	42.75
0.05	12.25	12.5	14.5	18.75	27.0	42.25
0.06	12.0	12.0	14.25	18.25	26.5	41.75
0.07	11.75	11.75	13.75	17.75	26.0	41.0
0.08	11.25	11.25	13.25	17.25	25.25	40.0
0.09	10.75	10.75	13.0	16.75	24.5	38.5
0.10	10.5	10.5	12.25	16.25	23.75	37.75
0.11	10.0	10.0	12.0	16.0	23.75	36.75
0.12	9.5	9.75	11.75	15.5	22.5	36.25
0.13	9.25	9.75	11.5	15.0	21.75	35.5
0.14	9.0	9.5	11.25	14.75	21.25	35.0
0.15	8.75	9.25	11.0	14.5	21.0	34.25
0.16	8.75	9.25	11.0	14.25	21.0	34.0
0.17	8.75	9.25	11.0	14.25	21.0	33.5
0.18	8.75	9.0	11.0	14.25	20.75	33.25
0.19	8.75	9.0	11.0	14.25	20.5	33.0
0.20	8.5	8.75	11.0	14.0	20.25	32.25
0.21	8.25	8.5	10.75	13.75	19.75	32.25
0.22	8.25	8.25	10.75	13.5	19.25	31.75
0.23	8.0	8.0	10.5	13.25	19.0	31.0

(Contd.)

T A B L E -5(Contd.)

0.24	7.75	7.75	10.25	12.75	18.5	30.25
0.25	7.5	7.5	10.0	12.25	18.0	29.5
0.26	7.0	7.0	9.75	11.75	17.5	28.75
0.27	6.75	6.75	9.5	11.25	17.0	28.0
0.28	6.5	6.5	9.25	10.75	16.25	27.0
0.29	6.0	6.0	8.75	10.25	15.75	25.75
0.30	5.25	5.25	8.25	10.0	15.25	24.75
0.31	4.5	4.5	7.75	9.25	14.5	23.75
0.32	3.75	3.75	7.25	8.5	13.75	22.0
0.33	3.25	3.25	6.75	8.0	13.25	21.0
0.34	2.5	2.5	6.25	7.0	12.5	19.75
0.35	2.0	2.0	5.5	6.25	12.0	18.5
0.36	1.5	1.5	5.0	5.75	11.25	17.25
0.37	0.75	0.75	4.25	5.0	10.25	15.75
0.38	0.5	0.5	3.75	4.5	9.5	15.0
0.39	0.0	0.0	3.25	4.0	9.0	13.75
0.40	+0.25	+0.25	2.75	3.5	8.0	12.5
0.41	0.5	0.5	2.25	2.75	7.25	11.5
0.42	0.75	0.75	1.75	2.25	6.5	10.5
0.43	1.0	1.0	1.25	2.0	5.75	8.75
0.44	1.0	1.25	0.75	1.5	5.0	7.75

(Contd.)

T A B L E -5(Contd.)

0.45	1.25	1.25	0.25	1.0	4.5	6.75
0.46	1.25	1.25	0.0	0.5	3.75	6.0
0.47	1.25	1.25	+0.25	0.0	3.25	5.0
0.48	1.25	1.25	0.5	+0.25	2.25	4.5
0.49	1.25	1.25	0.75	0.75	1.5	3.75
0.50	1.25	1.25	1.0	1.0	1.0	2.75
0.51	-	-	1.0	1.25	0.5	2.25
0.52	-	-	1.25	1.5	0.0	1.75
0.53	-	-	1.5	1.5	+0.5	1.0
0.54	-	-	1.5	1.75	0.75	0.75
0.55	-	-	1.5	1.75	1.0	0.25
0.56	-	-	-	1.75	1.5	0.0
0.57	-	-	-	2.0	1.5	+0.25
0.58	-	-	-	2.0	1.75	0.5
0.59	-	-	-	2.0	2.0	0.75
0.60	-	-	-	2.0	2.0	1.0
0.61	-	-	-	-	2.0	1.25
0.62	-	-	-	-	2.0	1.25
0.63	-	-	-	-	2.0	1.5
0.64	-	-	-	-	-	1.5

(Contd.)

T A B L E -5(Contd.)

0.65	-	-	-	-	1.75
0.66	-	-	-	-	1.75
0.67	-	-	-	-	1.75
0.68	-	-	-	-	1.75
0.69	-	-	-	-	1.75
0.70	-	-	-	-	1.75

Fig.6 Curve(I) Curve(II)Curve(III)Curve(IV)Curve(V) Curve(VI)

T A B L E -6.

Effect of temperature:

$[MoO(OH)(CN)_4]^{3-}$ = 1.0mM, KNO_3 = 0.1M, gelatin = 0.01%(h=81.25 cm.)

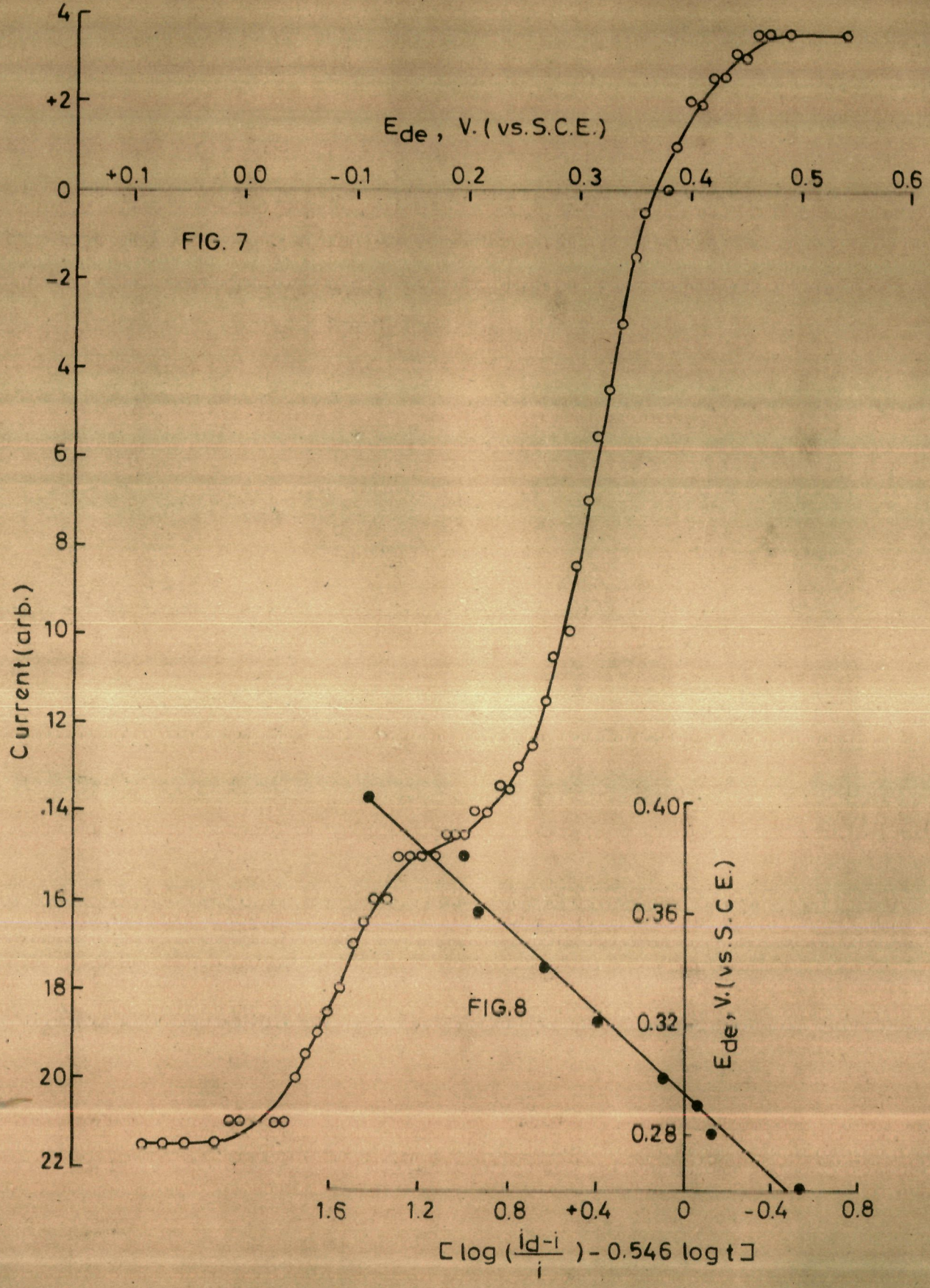
Temp.	i_d' (in μA)	i_d'' (μA)	Temperature coefficient (%) Ist Wave	Temperature coefficient (%) IInd wave
25	0.598	1.667	-	-
30	0.641	1.796	1.3	1.4
35	0.7268	2.138	1.2	1.7
40	0.898	2.779	1.4	1.7
45	1.197	3.890	1.4	1.6
50	1.71	5.912	1.4	1.6
Means	-	-	1.3	1.6

Figure 3 and 4 (Curves III) show the temperature dependence of the diffusion currents. Above 35°, the current values are seen to deviate from the straight lines of the plot; the current increases remarkably with the temperature, indicating a kinetically-controlled feature. This may be attributed to the probable disruption of the molybdate(VI) complex (see discussion) in solution. Below 35°c, the current changes of both the waves were linear with temperature; their coefficients being 1.3 and 1.6%/ degree respectively at 25°c. On the whole, no deformation of the waves with the temperature was observed.

Discussion

The linearity of i_d with depolarizer concentration, $h_{corr.}^{\frac{1}{3}}$ and temperature and the values of its temperature coefficients are in accord with the anodic limiting currents being controlled totally by diffusion upto 35°c.

The second step oxidation being irreversible, the kinetic parameters are included for the complete elucidation of irreversible processes. Since the determination of kinetic parameters is based on Koutecky's calculation, which are more accurately reproduced by measuring the maximum current,[11] the current at the end of drop-life has been recorded instead of the average current.


4
+2
0
-2
4
6
8
10
12
14
16
18
20
22
Current (arb.)
E_{de}, V. (vs. S.C.E.)
+0.1
0.0
-0.1
0.2
0.3
0.4
0.5
0.6
FIG. 7
0.40
0.36
0.32
0.28
E_{de}, V. (vs. S.C.E.)
FIG. 8
1.6
1.2
0.8
+0.4
0
-0.4
0.8
$[\log(\frac{i_d - i}{i}) - 0.546 \log t]$

The values of drop-time(t) were also measured at different potentials on the rising portion of the wave, such that i lies between 10 and 95% i_d, which are the approximate limits of the validity of the equation employed in the calculations. The data are given in table no.7.

T A B L E -7.

$[MoO(OH)(CN)_4]^{3-}$ = 1.0mM, KNO_3=0.1M, gelatin = 0.01%
(h= 81.25 cm) 25°c.

Potential (vs.SCE,V.)	Max. Current (arb.)	t(sec.)	Potential (vs.SCE.V.)	Max. Current (arb.)	t(sec.)
+0.09	-21.5	-	-0.20	-14.5	-4.80
0.08	21.5	-	0.21	14,0	4.81
0.07	21.5	-	0.22	14.0	4.813
0.06	21.5	-	0.23	13.5	4.815
0.05	21.5	-	0.24	13.5	4.817
0.04	21.5	-	0.25	13.0	4.82
0.03	21.5	-	0.26	12.5	4.823
0.02	21.5	-	0.27	11.5	4.825
0.01	21.5	-	0.28	10.5	4.826
0.00	21.0	4.62	0.29	10.0	4.828

(Contd.)

T A B L E -7(Contd.)

-0.01	22.0	-	0.30	8.5	4.83
0.02	22.0	-	0.31	7.0	4.831
0.03	21.0	-	0.32	5.5	4.831
0.04	21.0	-	0.33	4.5	4.832
0.05	20.0	-	0.34	3.0	4.833
0.06	19.5	-	0.35	1.5	4.835
0.07	19.0	-	0.36	0.5	4.837
0.08	18.5	-	0.38	0.0	4.839
0.09	18.0	-	0.39	1.0	4.840
0.10	17.0	4.72	0.40	2.0	4.842
0.11	16.5	-	0.41	2.0	4.843
0.12	16.0	-	0.42	2.5	4.845
0.13	16.0	-	0.43	2.5	4.846
0.14	15.0	4.75	0.44	3.0	4.847
0.15	15.0	4.75	0.45	3.0	4.848
0.16	15.0	4.76	0.46	3.5	-
0.17	15.0	4.77	0.47	3.5	-
0.18	14.5	4.78	0.48	3.5	-
0.19	14.5	4.79	0.49	3.5	-
0.20	-	-	0.50	3.5	4.851

Fig.7

The kinetic parameters have been calculated employing equations(16) and (17). The value of βn was obtained from the slope of the straight line plot $E_{d.e.}$ versus

$$\left[\log(i_d - i/i) - 0.546 \log t\right].$$

Such plot is shown in figure(8). The same plot gave the value of the intercept, $E_{\frac{1}{2}}^{o}$, which was used to calculate $k_{b,h}^{o}$, employing equation(17). The value $k_{b,h}$ was then calculated by means of the equation:

$$k_{b,h} = k_{b,h}^{o} \exp\left[\frac{\beta nF}{RT}(E + 0.2412)\right].$$

Diffusion coefficient was calculated by means of the Ilkovic equation taking n = 1. The value of $k_{b,h}$ was obtained at E = - 0.33V, the half wave potential of the second wave. The values are recorded in the following table:

T A B L E -8.

Apparent kinetic parameters of the electrode process for $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$ complex.

i_d (μA)	$Dx10^6$ ($cm^2 sec^{-1}$)	βn	$k_{b,h}^{o} x10^3$ ($cm.sec^{-1}$)	log $k_{b,h}$	$k_{b,h} x10^4$ ($cm.sec^{-1}$)
3.16_3	3.34_4	0.72_2	6.15_6	-3.29_6	5.06_0

Electrode Reaction: For the observed value of βn as 0.72; n is 1.4 if β = 0.5. This value of n is incorrect as it must be an integer. Thus one would conclude that n = 1.

This value has further been checked by plotting the first derivatives polarogram $\triangle i/\triangle E$ vs.E which shows only one peak. With this value of n, the second step reaction can be presumed to be

$$\left[Mo^{V}O(OH)(CN)_4\right]^{2-} \longrightarrow \left[Mo^{VI}O(OH)(CN)_4\right]^{1-} + e$$

as the first-step oxidation is a reversible, one electron transfer process. Thus, the over all electrode reaction may be described as:

$$\left[MoO(OH)(CN)_4\right]^{3-} \longrightarrow Mo^{4+} + OH^- + 4\,CN^- + O^{2-}$$

$$Mo^{IV} \xrightarrow{e} Mo^{V} \xrightarrow{e} Mo^{VI}$$

in which no chemical reaction seems to be appreciably involved at this temperature. Thus, throughout the oxidations, the complex is considered not to underago any structural change.

The $\left[MoO(OH)(CN)_4\right]^{3-}$ ion is hexa coordinated[12,13] with the electronic structure[14]

$$d^2d^0d^0\left[D^2Sp^3\right].$$

On the basis of atomic orbital[15] the electron transfer mechanism at the electrode surface may be given as:

$$d^2d^0d^0\left[D^2SP^3\right] \xrightarrow{-e} d^1d^0d^0\left[D^2SP^3\right] \xrightarrow{-e} d^0d^0d^0\left[D^2SP^3\right]$$

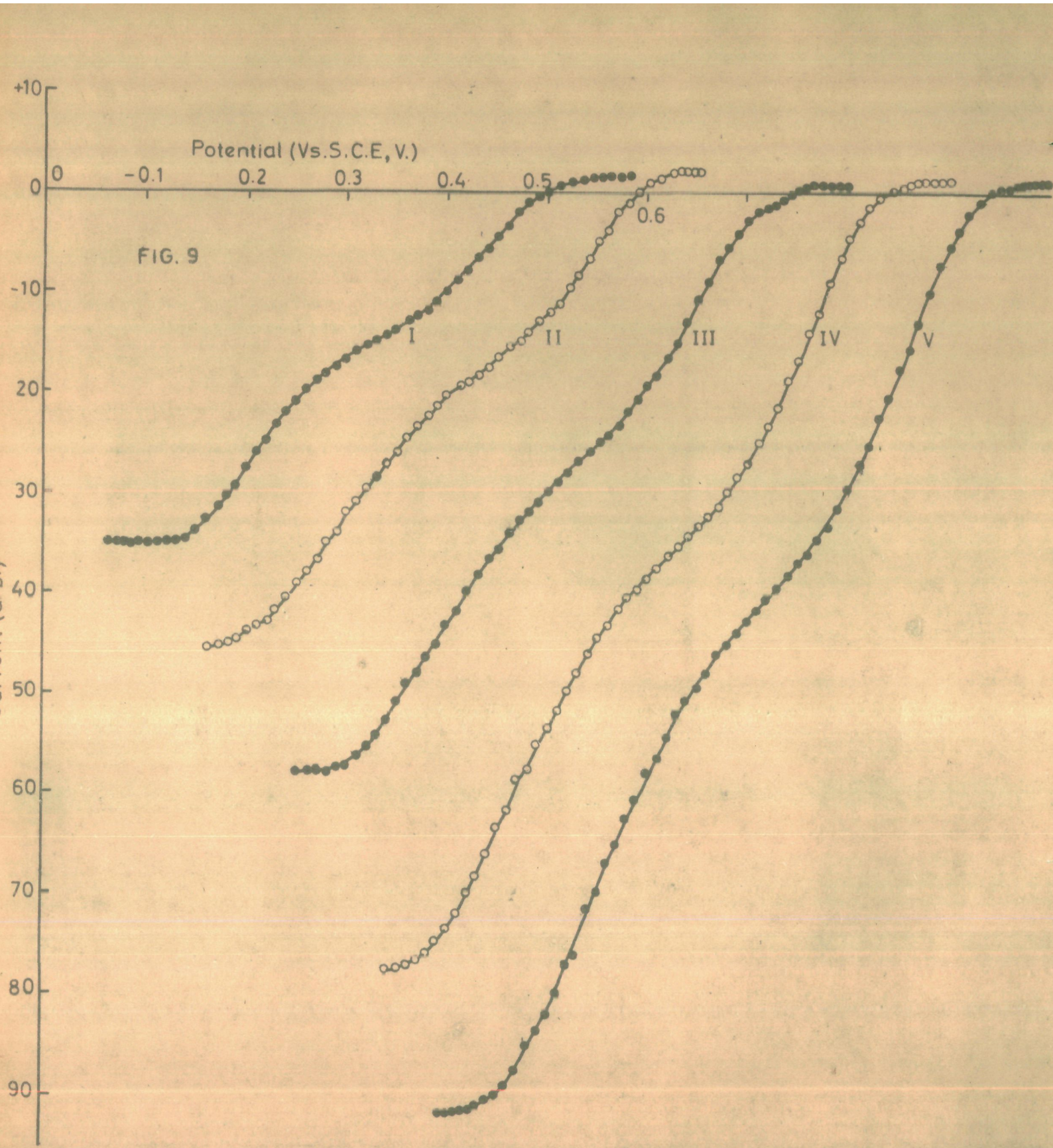

+10
0
-10
20
30
40
50
60
70
80
90
Potential (Vs.S.C.E, V.)
0
-0.1
0.2
0.3
0.4
0.5
0.6
I
II
III
IV
V

FIG. 9

(B) DIOXOTETRACYANO TUNGSTATE(IV) ION

Effect of depolarizer concentration:

Polarograms of different concentrations of TCT(6.05 to 17.5 mM) were recorded in the presence of 0.01% gelatin and 0.1M KNO_3 solutions. Two anodic waves were obtained. All the polarograms were taken at $0^{o}c$ as at higher temperatures the two waves tend to merge into one another.

The following table record the observations:

T A B L E -9.

[t=3.89 sec., m=1.411mg./sec.,h=43.0 cm.(Open circuit)]

Potential (vs.SCE,V.)	Current(arbitrary)				
	Concn.(mM)				
	6.05	8.77	11.70	14.60	17.50
0.0	-	-	-	-	-91.5
-0.01	-	-	-	-	91.5
0.02	-	-	-	-	91.5
0.03	-	-	-	-	91.0
0.04	-	-	-	-77.5	90.5
0.05	-	-	-58.0	77.5	90.0
0.06	-35.25	-45.5	58.0	77.25	89.0

(Contd.)

T A B L E -9.(Contd.)

0.07	35.25	45.5	58.0	76.5	87.5
0.08	35.25	45.25	58.0	76.0	85.25
0.09	35.25	44.75	57.5	74.75	83.5
0.10	35.25	44.0	57.5	73.5	82.0
0.11	35.25	43.5	56.25	72.0	79.75
0.12	35.25	43.0	55.5	70.0	77.0
0.13	35.25	41.75	54.25	68.25	76.0
0.14	34.75	40.5	52.75	66.0	71.5
0.15	34.0	39.25	51.0	63.5	69.5
0.16	32.75	37.75	49.25	61.75	66.75
0.17	31.75	36.75	48.25	58.75	65.0
0.18	30.5	35.0	46.5	57.75	62.5
0.19	29.25	34.0	45.25	55.25	60.5
0.20	27.25	32.0	43.25	53.75	57.75
0.21	26.25	31.0	42.0	52.0	56.5
0.22	24.25	29.75	40.0	50.0	54.25
0.23	23.25	28.5	38.5	48.0	52.0
0.24	22.75	27.25	36.75	46.25	50.75
0.25	21.0	26.25	35.75	44.5	49.5
0.26	20.0	24.5	34.25	43.25	48.0
0.27	19.0	23.5	32.75	41.75	46.0
0.28	18.25	22.5	32.0	40.5	45.0
0.29	17.5	21.5	31.0	39.75	44.0
0.30	17.0	20.5	30.0	38.5	42.75

(Contd.)

T A B L E -9(Contd.)

0.31	16.0	19.75	29.0	37.5	41.75
0.32	15.5	19.0	28.0	36.5	40.5
0.33	15.0	18.25	27.0	35.5	39.5
0.34	14.5	17.5	26.0	34.5	38.25
0.35	14.0	16.5	25.0	33.5	37.0
0.36	13.0	15.75	24.25	32.5	36.0
0.37	12.5	15.0	23.25	31.5	34.5
0.38	12.0	14.0	22.0	30.0	32.75
0.39	11.0	13.0	20.5	28.5	31.5
0.40	10.0	12.0	19.5	27.0	29.5
0.41	9.0	11.0	18.25	25.0	27.0
0.42	8.0	9.5	16.5	23.25	25.25
0.43	6.75	8.25	15.0	21.5	22.5
0.44	5.75	6.75	13.0	18.75	20.5
0.45	4.5	4.75	10.75	16.75	17.5
0.46	3.5	3.75	9.0	14.0	15.5
0.47	2.0	2.0	7.0	12.0	13.0
0.48	1.0	1.0	5.75	9.0	10.0
0.49	0.5	0.0	4.25	6.5	7.25
0.50	0.0	+1.0	3.0	4.75	5.25
0.51	+0.5	1.5	2.0	3.0	3.75
0.52	1.0	2.0	1.5	1.5	2.0

(Contd.)

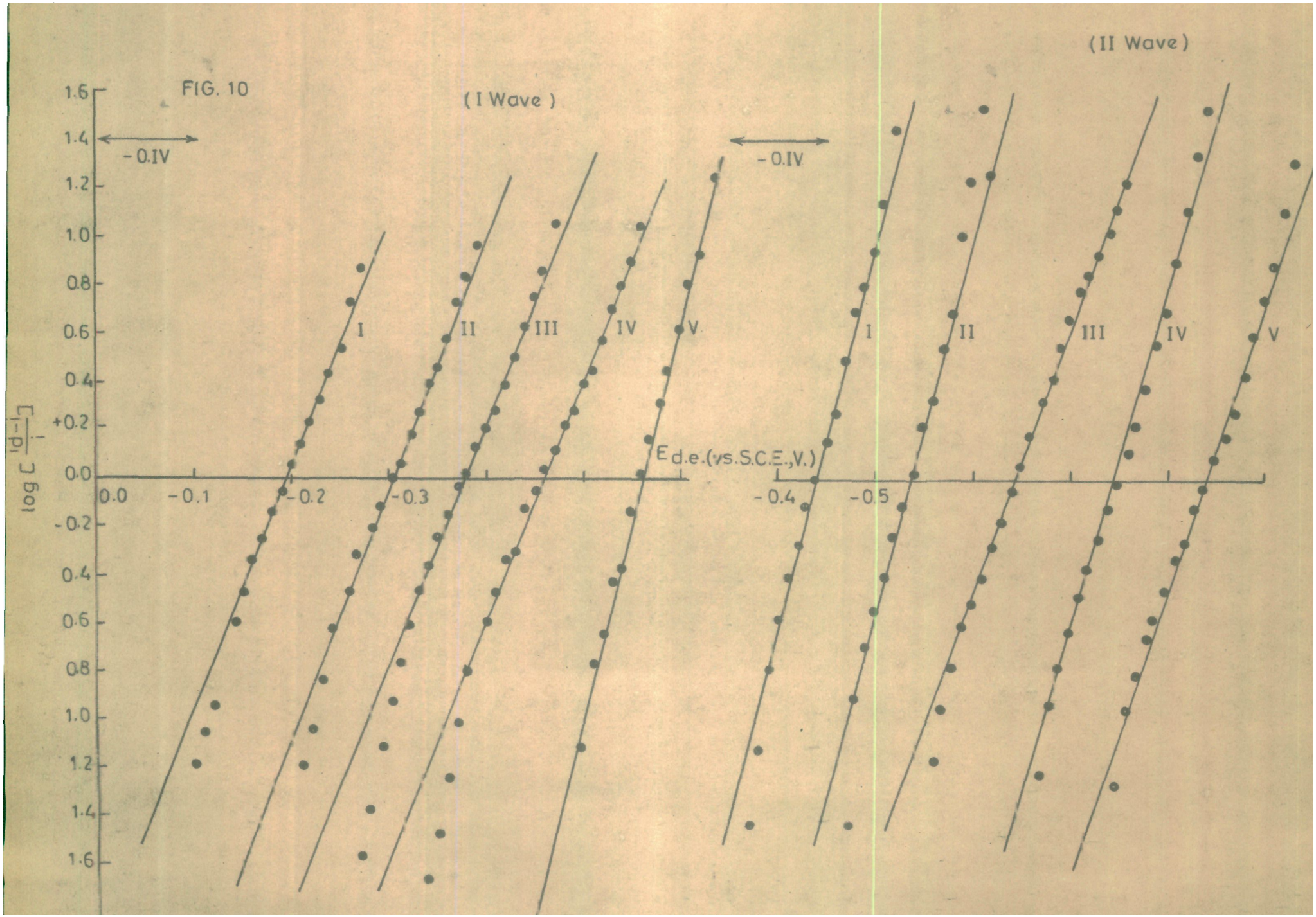


FIG. 10
(I Wave)
(II Wave)
-0.IV
-0.IV
I
II
III
IV
V
I
II
III
IV
V
E d.e.(vs.S.C.E.,V.)
log [i/(i-pi)]
1.6
1.4
1.2
1.0
0.8
0.6
0.4
+0.2
0.0
-0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0.0
-0.1
-0.2
-0.3
-0.4
-0.5

T A B L E -9(Contd.)

0.53	1.0	2.0	1.0	0.5	1.0
0.54	1.5	2.0	0.5	0.0	0.0
0.55	1.5	2.0	0.0	+0.5	+0.5
0.56	1.5	-	+0.5	0.5	0.5
0.57	1.5	-	0.5	0.0	1.0
0.58	1.5	-	0.5	1.0	1.0
0.59	1.5	-	0.5	1.0	1.0
0.60	1.5	-	0.5	1.0	1.0
Fig.9	Curve(I)	Curve(II)	Curve(III)	Curve(IV)	Curve(V)

The reversibility of the electrode reaction was tested by plotting $\log(i_d - i/i)$ versus $E_{d.e.}$ Fig.(10) shows that the first step oxidation is irreversible (as the slope was always found to be in the range of 0.09), while the second step oxidation is reversible (as the slope was found in the range of 0.055) corresponding to a loss of one electron.

The following table shows the test for the linearity of the wave heights with the depolarizer concentration.

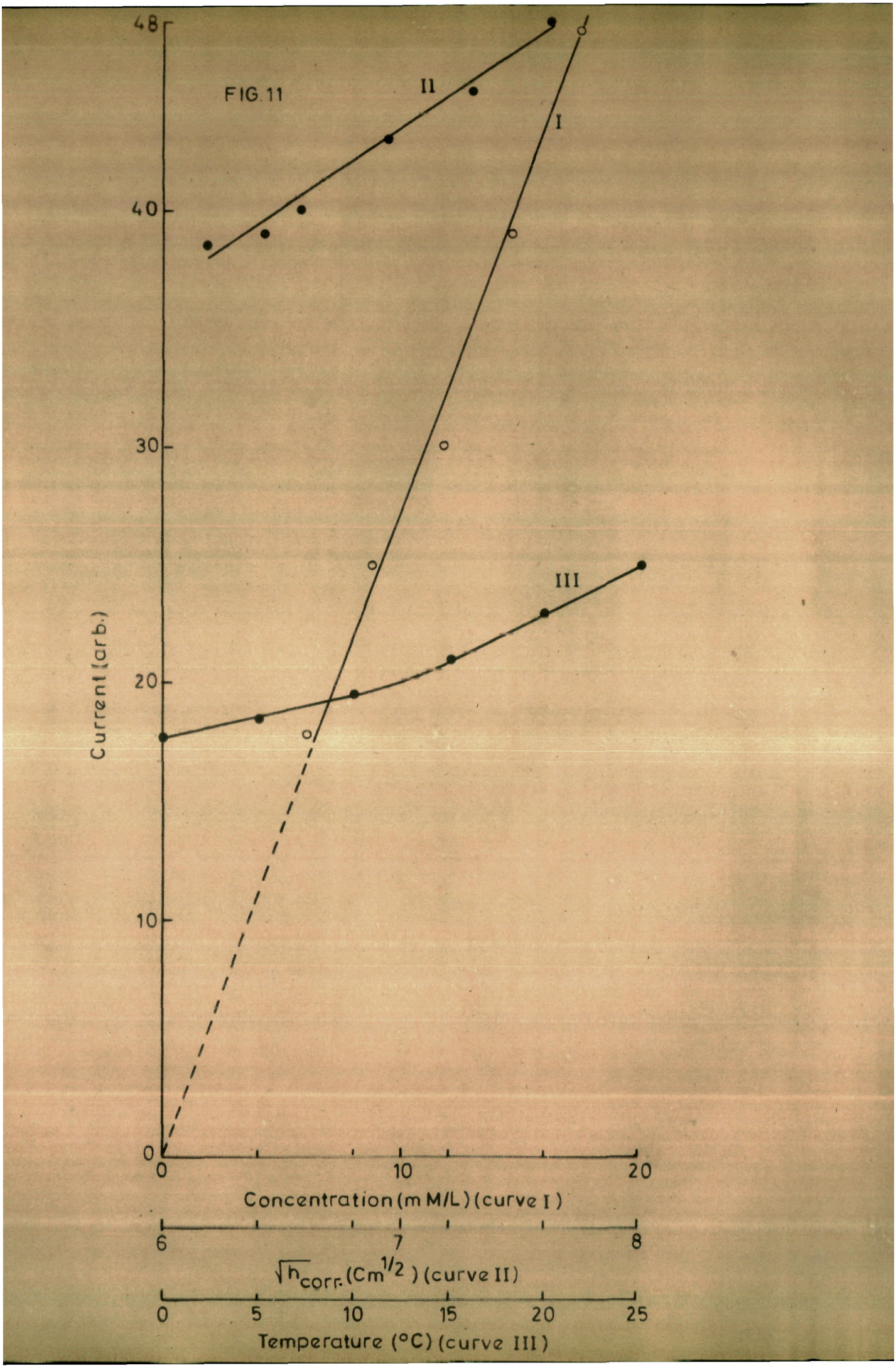


FIG. 11
48
40
30
20
10
0
II
I
III
Current (arb.)
0
10
20
Concentration (m M/L) (curve I)
6
7
8
$\sqrt{h}_{corr.}$ ($Cm^{1/2}$) (curve II)
0
5
10
15
20
25
Temperature (°C) (curve III)

FIG. 12

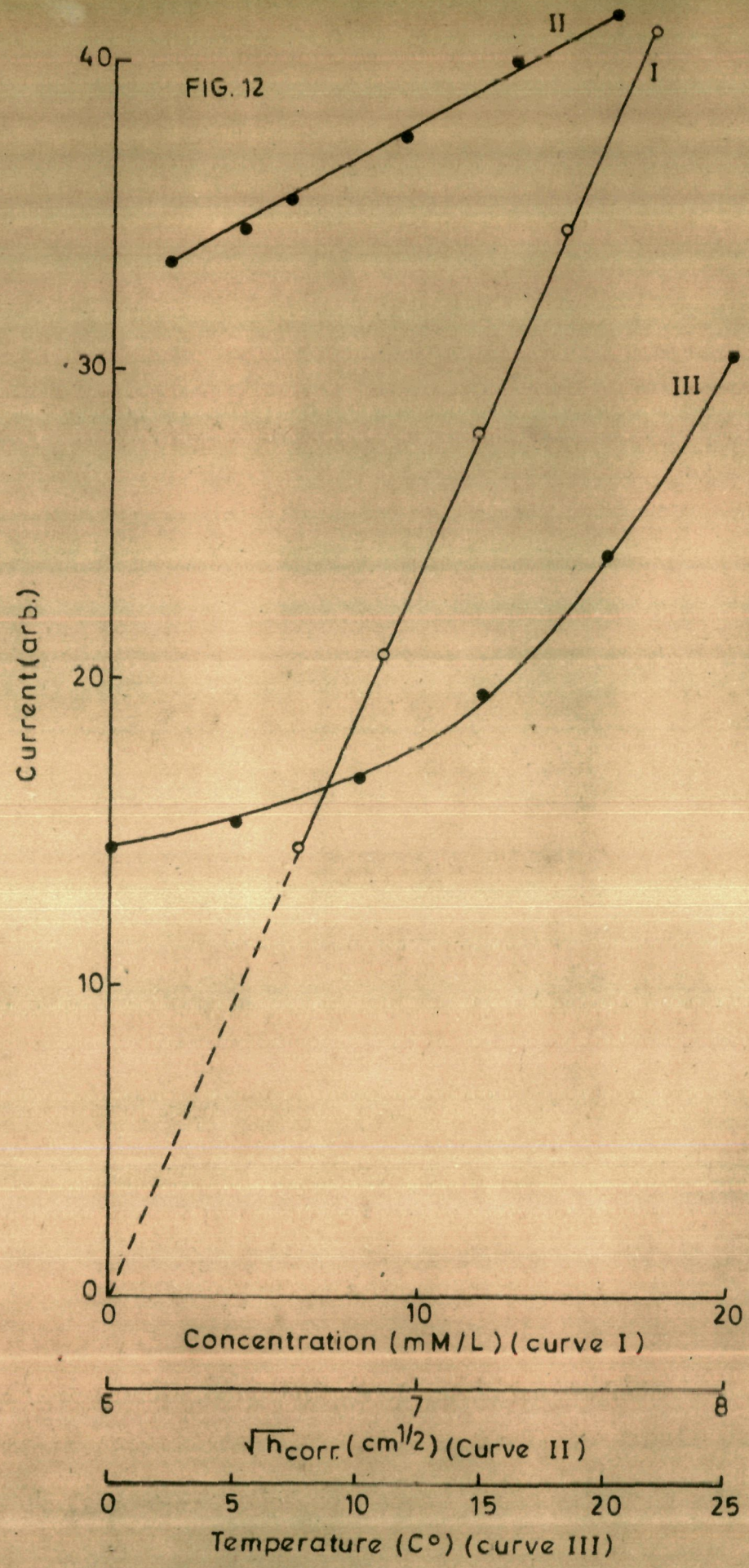

II
I
III
40
30
20
10
0
Current (arb.)
0
10
20
Concentration (mM/L) (curve I)
6
7
8
$\sqrt{h_{corr.}}$ ($cm^{1/2}$) (Curve II)
0
5
10
15
20
25
Temperature (C°) (curve III)

TABLE -10.

Concn. of TCT (mM)	i_d (μA)	i_d/c	$I = i_d/cm^{\frac{2}{3}}t^{1/6}$	$-E_{\frac{1}{2}}$ (vs.SCE,V)
		For first-wave		
6.05	3.035	0.513	0.323	0.200
8.77	4.275	0.487	0.306	0.195
11.70	5.130	0.438	0.276	0.200
14.60	6.669	0.456	0.288	0.185
17.50	8.023	0.467	0.294	-
Means	-	0.472_4	0.297_4	
		For second wave		
6.05	2.479	0.410	0.259	-
8.77	3.078	0.351	0.221	0.435
11.70	4.788	0.409	0.258	0.435
14.60	5.899	0.404	0.255	0.440
17.50	7.011	0.403	0.253	0.440
Means	-	0.395_3	0.249_1	-

The above table shows that the values of 'i_d/c' and 'I' are almost constant within the experimental error. This clearly indicate that 'i_d' is proportional to TCT concentration.

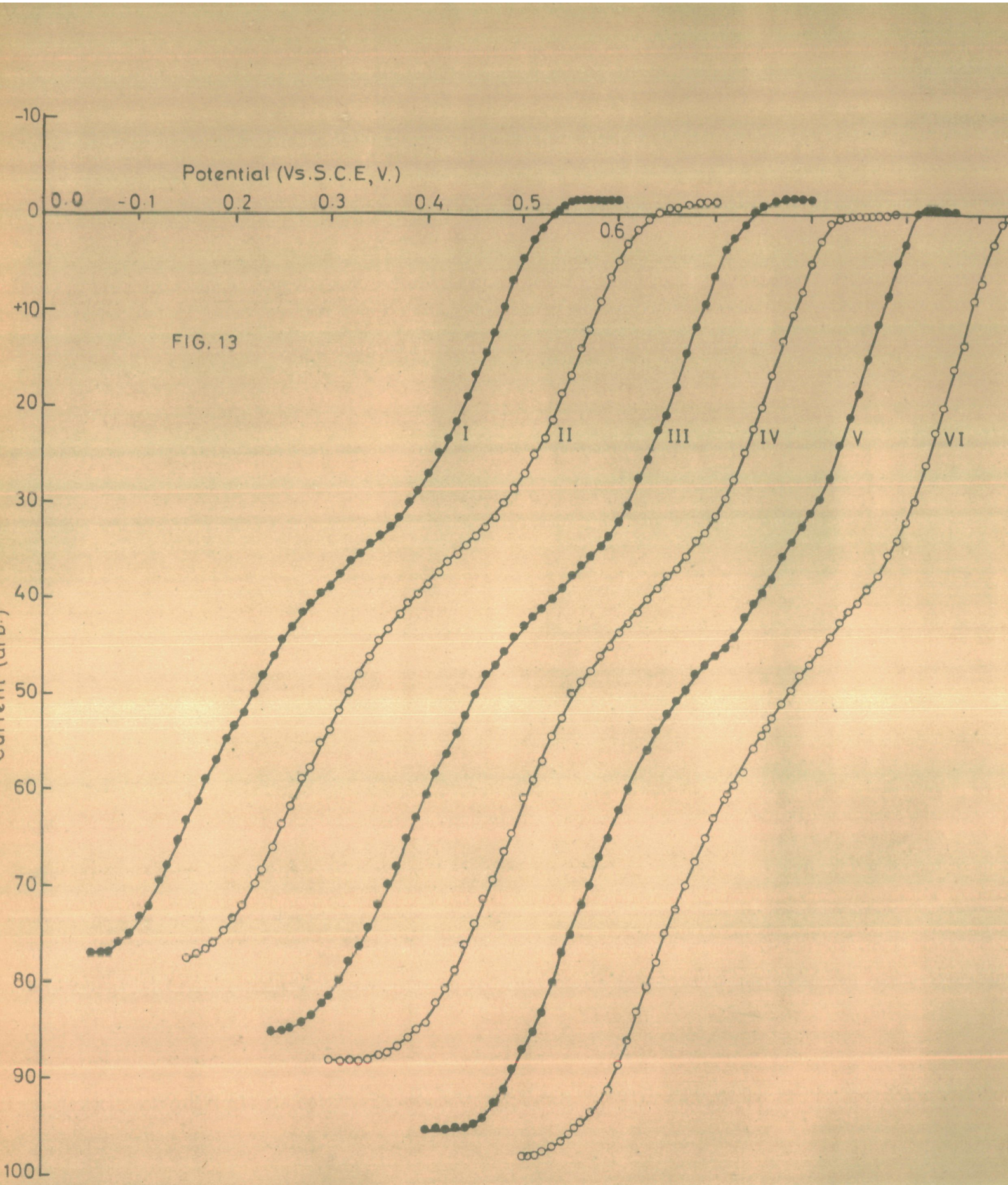

Potential (Vs.S.C.E, V.)
0.0
-0.1
0.2
0.3
0.4
0.5
0.6
-10
0
+10
20
30
40
50
60
70
80
90
100
I
II
III
IV
V
VI

FIG. 13

The relation between the diffusion currents and concentrations (Figs.11 and 12, curves I) clearly show that both the lines pass through origin. The half wave potentials of both the waves were found to be independent of depolarizer concentration. The linearity of wave height with TCT concentration provide a rapid and precize method for polarographic determination taking into consideration either of the two waves.

Effect of drop-time:

A series of polarograms of 14.6mM TCT were obtained at different heights of mercury column at 0°c. The following table recorded the observations:

T A B L E -11.

Potential (vs.SCE,V)	Current(arbitrary) Heights (cm.)					
	40	43	45	50	55	60
0.0	-	-	-	-88.0	-95.0	-98.0
-0.01	-	-	-	88.0	95.0	98.0
0.02	-	-	-	88.0	95.0	97.5
0.03	-	-	-	88.0	95.0	97.0
0.04	-	-	-85.0	88.0	95.0	96.5

(Contd.)

TABLE -11(Contd.)

0.05	-77.0	-77.5	85.0	87.5	94.5	95.5
0.07	77.0	76.5	84.25	86.5	92.5	93.5
0.08	76.0	76.0	83.5	85.75	91.0	92.0
0.09	75.0	74.75	82.25	84.75	89.0	91.0
0.10	73.5	73.5	81.25	84.25	87.0	88.5
0.11	72.0	72.0	79.75	82.0	85.0	86.0
0.12	69.5	70.0	77.75	80.5	83.0	83.0
0.13	68.0	68.25	76.25	78.5	80.0	80.5
0.14	65.5	66.0	74.25	76.0	77.0	78.0
0.15	63.0	63.5	72.0	74.0	75.0	75.0
0.16	61.5	61.75	70.0	71.25	72.0	72.5
0.17	59.0	58.75	68.0	69.5	70.0	70.0
0.18	57.0	57.75	65.0	66.5	67.0	67.5
0.19	54.75	55.25	63.0	64.5	65.0	65.0
0.20	53.25	53.75	60.25	61.0	62.0	63.0
0.21	52.0	52.0	58.75	59.0	60.0	61.0
0.22	50.0	50.0	56.25	57.0	57.0	59.5
0.23	48.25	48.0	54.5	54.5	56.0	58.0
0.24	46.0	46.25	52.5	52.5	54.0	55.5
0.25	44.5	44.5	50.0	50.0	52.0	54.5
0.26	43.0	43.25	48.0	48.5	50.5	52.0
0.27	41.5	41.75	47.0	47.5	49.5	51.0

(Contd.)

T A B L E -11(Contd.)

0.28	40.5	41.5	45.5	46.0	48.0	49.5
0.29	39.5	39.75	44.0	45.0	47.0	48.0
0.30	39.0	38.5	43.0	43.5	46.0	47.0
0.31	37.5	37.5	42.0	43.5	45.0	44.5
0.32	36.0	36.0	41.0	41.5	44.0	44.0
0.33	35.5	35.5	40.0	40.0	42.0	42.5
0.34	34.5	34.5	39.0	39.0	40.5	41.5
0.35	33.5	33.5	37.5	37.75	39.5	40.5
0.36	32.5	32.5	36.5	37.0	38.0	39.0
0.37	31.5	31.5	35.5	35.5	35.5	37.5
0.38	30.0	30.0	34.5	34.0	34.0	35.5
0.39	28.75	28.5	33.25	33.0	32.5	34.0
0.40	27.0	27.0	32.0	31.5	31.0	32.0
0.41	25.0	25.0	30.25	29.5	29.5	30.0
0.42	23.5	23.25	27.25	27.5	27.5	26.0
0.43	21.5	21.5	25.5	24.5	24.0	22.5
0.44	19.0	18.75	22.75	22.25	21.0	20.0
0.45	16.5	16.75	20.75	20.0	18.5	16.0
0.46	14.0	14.0	17.75	16.75	15.5	13.5
0.47	12.0	12.0	14.25	13.0	11.5	9.0

(Contd.)

T A B L E -11(Contd.)

0.48	9.5	9.0	11.5	10.5	8.5	7.0
0.49	6.75	6.5	9.25	8.0	5.0	3.0
0.50	4.75	4.75	6.5	5.0	3.0	1.0
0.51	2.5	3.0	3.75	2.75	0.0	0.0
0.52	1.5	1.5	2.25	0.5	+0.5	0.0
0.53	0.0	0.5	1.0	0.0	0.5	0.0
0.54	+1.0	0.0	+0.5	0.0	0.5	0.0
0.55	1.5	+0.5	1.0	0.0	0.5	0.0
0.56	1.5	0.5	1.5	0.0	0.5	-
0.57	1.5	1.0	1.5	0.0	0.5	-
0.58	1.5	1.0	1.5	0.0	0.5	-
0.59	-	1.0	-	-	-	-
0.60	-	1.0	-	-	-	-

Fig.13 Curve(I) Curve(II) Curve(III) Curve(IV) Curve(V) Curve(VI)

TABLE-12.

Effect of mercury pressure:

$[WO_2(CN)_4]^{4-}$ = 14.6mM, KNO_3 = 0.1N, gelatin = 0.01% (0°C).

h_{Hg} (cm)	m (mg./sec.)	t (sec.)	mt (mg.)	$h_{corr.}$ (cm.)	$h^{\frac{2}{3}}_{corr.}$ ($cm.^{\frac{2}{3}}$)	$100m/h_{corr}$	i_d' (μA)	i_d'' (μA)	$i_d'/h^{\frac{2}{3}}_{corr.}$	$i_d''/h^{\frac{2}{3}}_{corr.}$
40.0	1.331	4.12	5.524	38.24	6.184	34.80	6.58_3	5.72_8	0.919	0.926
43.0	1.414	3.89	5.485	41.24	6.421	34.22	6.66_9	5.89_9	1.039	0.918
45.5	1.481	3.70	5.480	43.24	6.575	34.26	6.84_0	6.07_0	1.040	0.923
50.0	1.639	3.35	5.491	48.24	6.945	33.98	7.35_3	6.41_2	1.059	0.923
55.0	1.829	3.00	5.487	53.24	7.295	34.37	7.69_5	6.84_0	1.054	0.937
60.0	1.992	2.75	5.478	58.24	7.632	34.19	8.20_8	7.09_6	1.075	0.929
Means	-	-	5.490_8	-	-	34.30_3	-	-	1.031	0.926

Back pressure = $3.1/(mt)^{\frac{1}{3}}$ = $3.1/(5.49)^{\frac{1}{3}}$ = 1.76 cm. of Hg.

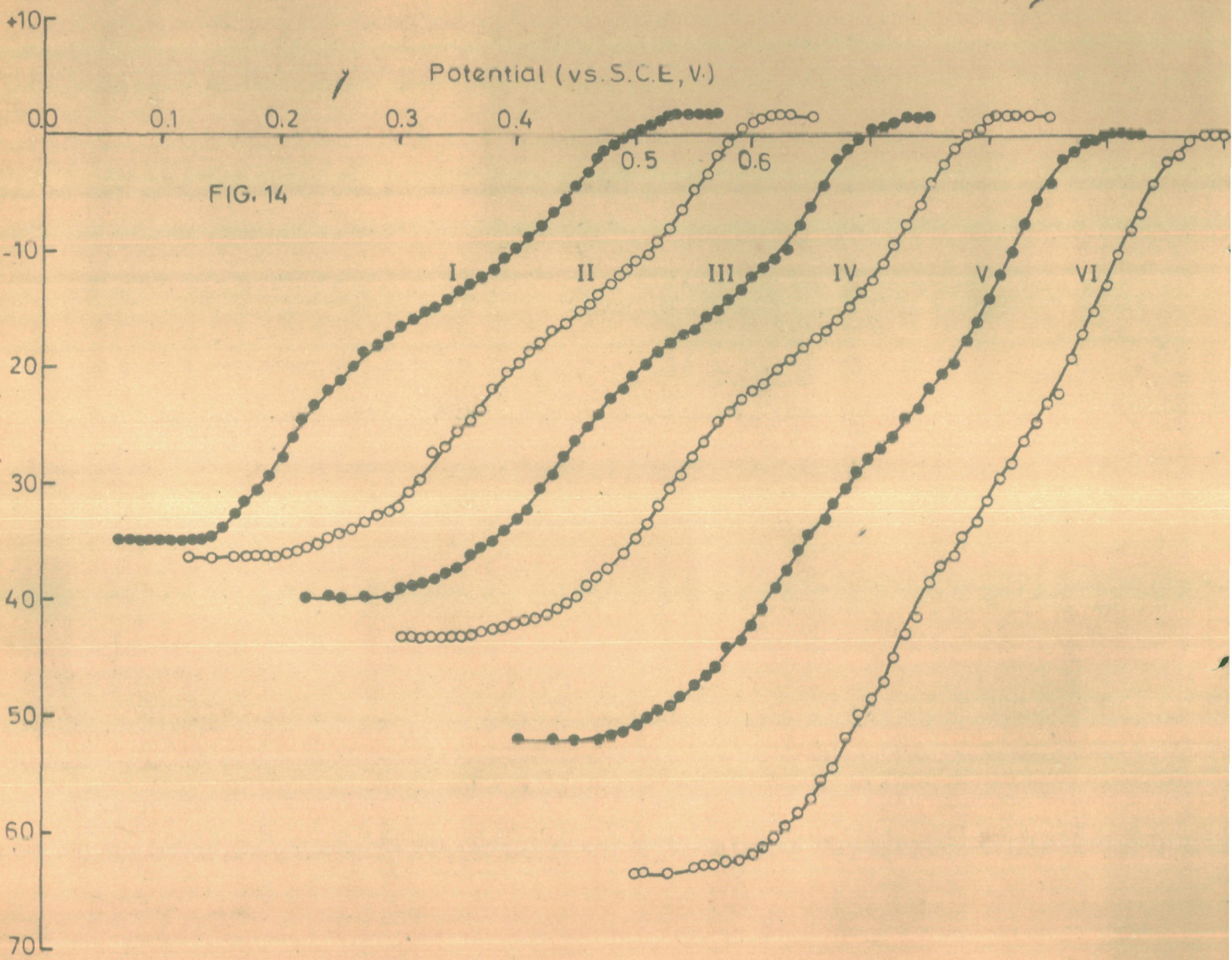

+10
Potential (vs. S.C.E, V.)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
-10
20
30
40
50
60
70
I
II
III
IV
V
VI

FIG. 14

The diffusion currents of the first as well as the second steps were found to be proportional to the square-root of the heights of mercury column on d.m.e. (Figs.11 and 12, curve II) and the values of $i_d/h^{\frac{1}{2}}$ corr. were constant irrespective of the mercury pressure (table 12). This shows that height of both the anodic waves is solely controlled by diffusion factor.

Effect of temperature:

A solution of 6.05mM TCT was polarographed in the temperature range from 0 to 25°c. The observations are recorded in table no.13 and $i_{d,s}$, temperature -coefficients values are given in table no.14.

T A B L E -13.

[t= 3.89 sec., m = 1.414 mg./sec., h=43.0 cm.(open circuit)].

Potential (vs.SCE,V)	Current(arbitrary) Temperatures(C°)					
	0	5	10	15	20	25
0.0	-	-	-	-43.5	-52.0	-63.5
-0.01	-	-	-	43.5	52.0	63.5
0.02	-	-36.5	-40.0	43.5	52.0	63.5

(Contd.)

T A B L E -13(Contd.)

0.03	-	36.5	40.0	43.5	52.0	63.5
0.04	-	36.5	40.0	43.5	52.0	63.5
0.05	-	36.5	40.0	43.5	52.0	63.5
0.06	-35.25	36.5	40.0	43.25	52.0	63.0
0.07	35.25	36.5	40.0	43.0	52.0	62.75
0.08	35.25	36.5	40.0	42.75	51.5	62.5
0.9	35.25	36.5	40.0	42.5	51.25	62.5
0.10	35.25	36.5	39.5	42.0	51.0	62.0
0.11	35.25	36.25	39.25	41.75	50.25	61.5
0.12	35.25	36.0	39.0	41.5	49.5	60.5
0.13	35.25	35.5	38.5	41.0	49.0	59.75
0.14	34.75	34.75	38.0	40.5	48.25	58.5
0.15	34.0	34.5	37.5	39.75	47.5	57.0
0.16	32.75	34.0	36.5	38.5	46.5	55.5
0.17	31.75	33.5	35.75	38.0	45.75	54.25
0.18	30.5	32.75	35.25	37.5	44.0	52.0
0.19	29.25	32.5	34.25	36.0	43.25	50.0
0.20	27.75	32.0	33.25	34.75	42.0	48.5
0.21	26.25	31.0	32.25	33.75	40.5	47.0
0.22	24.75	30.0	30.5	32.0	39.0	45.0
0.23	23.5	27.75	29.5	30.5	37.5	42.75

(Contd.)

T A B L E - 13(Contd.)

0.24	22.5	27.0	28.0	29.5	35.75	41.5
0.25	21.0	25.75	26.5	28.0	34.25	38.75
0.26	20.0	24.75	25.5	26.5	33.0	37.25
0.27	19.0	23.75	24.25	25.0	31.75	36.25
0.28	18.25	22.0	23.0	24.0	30.5	24.5
0.29	17.5	20.5	22.0	23.0	29.0	33.0
0.30	17.0	20.0	21.0	22.0	28.0	31.5
0.31	16.0	18.75	20.0	21.5	27.0	29.5
0.32	15.5	18.0	19.0	20.5	26.0	28.25
0.33	15.0	17.0	18.0	19.5	24.25	26.5
0.34	14.5	16.5	17.5	18.5	23.5	24.75
0.35	14.0	15.5	17.0	17.75	21.75	23.0
0.36	13.0	15.0	16.0	17.0	20.5	22.25
0.37	12.5	14.0	15.25	16.0	19.5	19.25
0.38	12.0	13.0	14.5	15.0	17.5	17.25
0.39	11.0	12.0	13.5	13.75	16.0	15.0
0.40	10.0	11.0	12.5	12.75	14.0	12.75
0.41	9.0	10.5	11.5	11.0	12.0	10.25
0.42	8.0	9.5	11.0	9.5	10.0	8.25
0.43	6.75	8.25	10.0	7.75	7.75	6.75
0.44	5.75	6.75	8.0	6.25	5.75	4.25
0.45	4.5	4.75	6.25	4.25	4.25	2.25

(Contd.)

T A B L E -13(Contd.)

0.46	3.5	3.5	4.5	2.75	2.25	1.5
0.47	2.0	2.0	2.25	1.25	1.5	0.5
0.48	1.0	1.0	1.5	0.0	0.75	0.25
0.49	0.5	+0.5	0.5	+0.5	0.5	0.0
0.50	0.0	1.0	+0.5	1.5	0.0	0.0
0.51	+0.5	1.5	0.5	1.5	0.0	0.0
0.52	1.0	1.5	1.0	1.5	0.0	0.0
0.53	1.0	1.5	1.5	1.5	0.0	0.0
0.54	1.5	1.5	1.5	1.5	0.0	0.0
0.55	1.5	1.5	1.5	-	-	-
0.56	1.5	1.5	1.5	-	-	-
0.57	1.5	1.5	1.5	-	-	-
0.58	-	-	-	-	-	-
0.59	-	-	-	-	-	-
0.60	-	-	-	-	-	-

Fig.14 Curve(I)Curve(II)Curve(III)Curve(IV)Curve(V)Curve(VI)

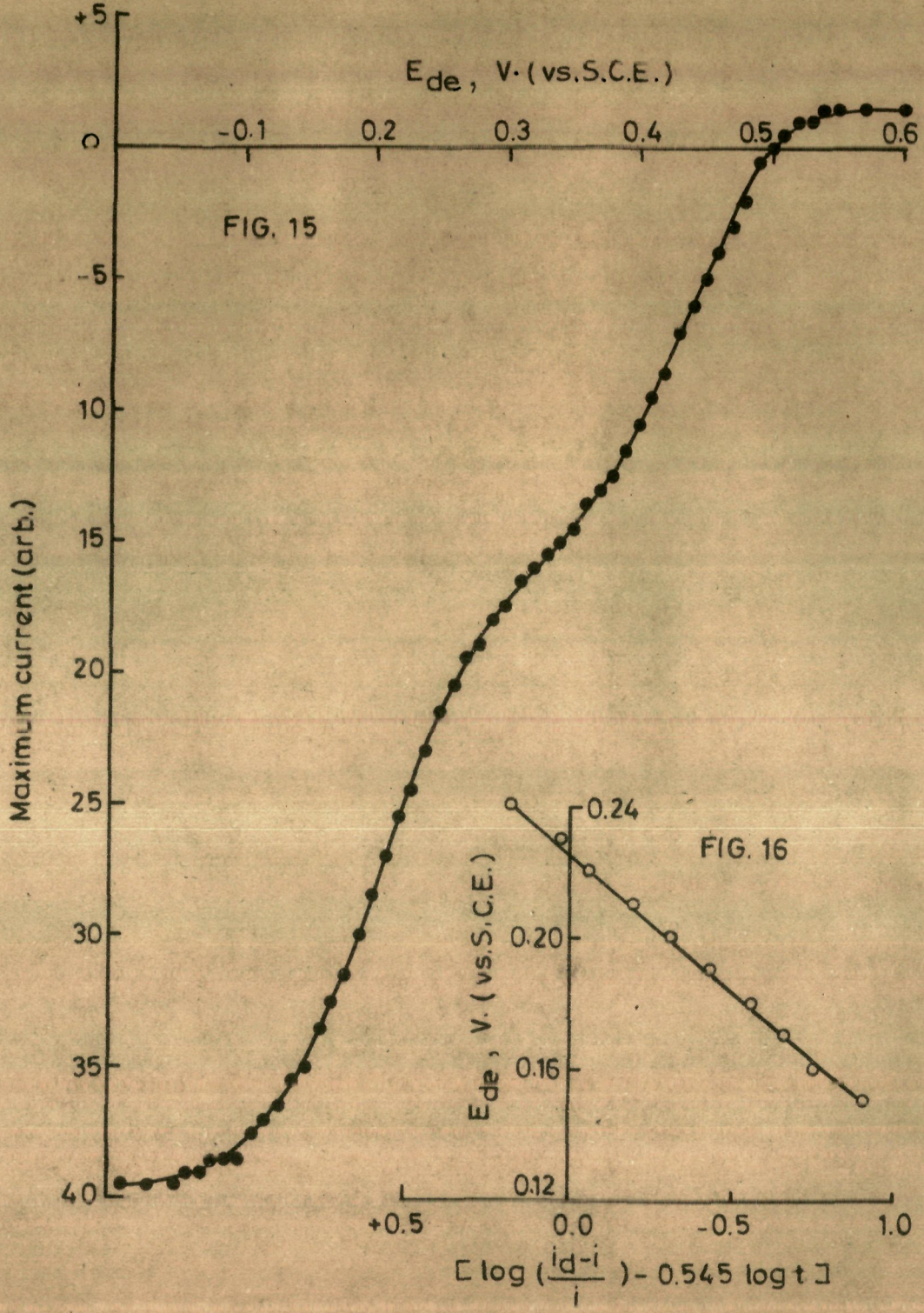
TABLE - 14.

Effect of temperature:

$[WO_2(CN)_4]^{4-}$ =6.05mM, KNO_3=0.1M, gelatin=0.01%, (h=43.0 cm)

Temp.	i_d(μA)	i_d"(μA)	Temperature coefficient% Ist wave	Temperature coefficient% IInd wave
0	3.035	2.479	-	-
5	3.163	2.607	0.8	1.0
10	3.344	2.778	0.5	0.6
15	3.591	3.334	0.5	1.2
20	3.931	4.104	0.4	0.9
25	4.275	5.215	0.3	0.9
Means	-	-	0.5_0	0.9_2

The values of temperature coefficients of i_d at these temperatures indicate that the height of both the waves of TCT, is controlled by diffusion factor. Figures 11 and 12 (curves III) show the dependence of i_d's on temperature. Above 10°C, the current values were seen to deviate from the straight lines of the plot; the current increases remarkedly with temperature, indicating a kinetically-controlled characteristic. This may be attributed to the probable disruption of the tungstate(VI) complex which is finally formed in solution. Below 10°C, the current changes of both the waves were linear with temperature.


+5
0
-5
10
15
20
25
30
35
40
Maximum current (arb.)
E_{de}, V. (vs.S.C.E.)
-0.1
0.2
0.3
0.4
0.5
0.6
FIG. 15
0.24
0.20
0.16
0.12
E_{de}, V. (vs.S.C.E.)
FIG. 16
+0.5
0.0
-0.5
1.0
$[\log(\frac{i_d - i}{i}) - 0.545 \log t]$

DISCUSSION

The constancy of $i_d/h^{\frac{1}{2}}_{corr.}$ and the values of temperature coefficients of i_d are in accord with the anodic limiting currents being diffusion-controlled upto 10°C.

As already described, the first step oxidation is irreversible. The kinetic parameters must be included for the complete elucidation of irreversible processes. The determination of these parameters is based on the same method as described in the case of TCM. The maximum current and drop-time with potential was recorded for a solution of 6.05mM TCT at 0°C. Following table records these observations:

TABLE - 15.

$[WO_2(CN)_4]^{4-}$ = 6.05mM, KNO_3= 0.1M, gelatin=0.01%(0°C).

Potential vs.SCE,V)	Maximum current	t(sec.)	Potential (vs.SCE,V)	Maximum current	t(sec.)
-0.0	-40.5	-	0.38	12.5	-
0.06	39.0	-	0.39	11.5	-
0.07	39.0	-	0.40	10.5	-

(Contd.)

TABLE - 15.(Contd.)

0.08	38.5	-	0.41	9.5	-
0.09	38.5	-	0.42	8.5	-
0.10	38.5	4.0	0.43	7.0	-
0.11	37.5	-	0.44	6.0	-
0.12	37.0	-	0.45	5.0	-
0.13	36.5	4.02	0.46	4.0	-
0.14	35.5	4.02	0.47	3.0	-
0.15	35.0	4.03	0.48	2.0	-
0.16	33.5	4.03	0.49	0.5	-
0.17	32.5	4.04	0.50	0.0	-
0.18	31.5	4.05	0.51	40.5	-
0.19	30.0	4.06	0.52	1.0	-
0.20	28.5	4.067	0.53	1.0	-
0.21	27.0	4.07	0.54	1.5	-
0.22	25.5	4.073	0.55	1.5	-
0.23	24.5	4.075	0.56	1.5	-
0.24	23.0	4.076	0.57	1.5	-
0.25	21.5	4.076	0.58	1.5	-
0.26	20.5	4.077	0.59	1.5	-
0.27	19.5	4.078	0.60	1.5	-

(Contd.)

T A B L E - 15(Contd.)

0.28	19.0	4.079	0.48	2.0	-
0.29	18.0	-	0.49	0.5	-
0.30	17.5	-	0.50	0.0	-
0.31	16.5	-	0.51	45.0	-
0.32	16.0	-	0.52	1.0	-
0.33	15.5	-	0.53	1.0	-
0.34	15.0	-	0.54	1.5	-
0.35	14.5	-	0.55	1.5	-
0.36	13.5	-	0.56	1.5	-
0.37	13.0	-	0.57	1.5	-
0.38	12.5	-	0.58	1.5	-
0.39	11.5	-	0.59	1.5	-
0.40	10.5	-	0.60	1.5	-
0.41	9.5	-	Fig.15		
0.40	8.5	-			
0.43	7.0	-			
0.44	6.0	-			
0.45	5.0	-			
0.46	4.0	-			
0.47	3.0	-			

Equations(16) and (17) were employed for the determination of kinetic parameters in the case of TCM at 25°C. At 0°C these equations can be written as:

$$E_{d.e} = E_{\frac{1}{2}}^{o} + \frac{0.0497}{\beta n}\left[\log (i_d - i/i) - 0.545 \log t\right] \qquad (18)$$

where $E_{\frac{1}{2}}^{o} = -0.2602 - \frac{0.05419}{\beta n} \log \frac{1.349\, k_{b,h}^{o}}{D^{\frac{1}{2}}}$ (19)

by using 0.2602 volt as the potential of saturated calomel electrode at 0°C.[16]

The kinetic parameters have been calculated employing equations(18) and (19). The value of βn was obtained by equating the slope (0.083) of the straight line plot $E_{d.e}$ versus.

$$\left[\log(i_d - i/i) - 0.545 \log t\right]$$

(Fig.16) with $0.0497/\beta n$. The same plot gave the intercept $E_f^o = -0.225V$ which was used to calculate $k^o_{b,h}$, employing equation(19). The value of $k_{b,h}$ was calculated by means of the equation,

$$k_{b,h} = k^o_{b,h} \exp\left[\frac{\beta nF}{RT}(E + 0.2602)\right] \quad \ldots\ldots\ldots \quad (20)$$

Diffusion coefficient was obtained by means of Ilkovic equation taking n = 1. The value of $k_{b,h}$ was calculated at E = - 0.435V, the half wave potential of the second wave. The kinetic parameters are summarized in the following table.

T A B L E -16.

i_d (μA)	$Dx10^7$ ($cm^2 sec.^{-1}$)	βn	$k^o_{b,h} x\ 10^4$ ($cm. sec.^{-1}$)	$\log k_{b,h}$	$k_{b,h} x10^5$ ($cm. sec.^{-1}$)
3.67_6	4.00_6	0.59_9	1.91_6	-4.23_5	5.81_7

Electrode-reaction:

As the value of βn is 0.59, n = 1.2 with β = 0.5, which must be an integer. Thus one would conclude that n=1. This value has further been checked by plotting the first derivative polarogram $\triangle i/\triangle E$ vs.[which shows only one peak. With this value of n, the first-step reaction can be presumed as:

$$\left[WO_2^{IV}(CN)_4\right]^{4-} \longrightarrow \left[WO_2^{V}(CN)_4\right]^{3-} + e$$

The second step oxidation has already been found to be reversible, one electron transfer process. Therefore,the overall electrode reaction may be described as:

$$\left[W^{IV}O_2(CN)_4\right]^{4-} \longrightarrow W^{4+} + 4\ CN^- + 2O^{2-}$$

$$W^{IV} \xrightarrow{e} W^{V} \xrightarrow{e} W^{VI}$$

in which no chemical reaction seems to be appreciably involved at this temperature. Thus, throughout the oxidations, the complex is considered not be undergo any structural change.

Just like $\left[Mo^{IV}O(OH)(CN)_4\right]^{3-}$; $\left[W^{IV}O_2(CN)_4\right]^{4-}$ ion is also hexacoordinated[12,13] with the electronic structure[14]:

$$d^2d^0d^0\ \left[D^2SP^3\right]$$

On the basis of atomic orbital method[15] the electron transfer mechanism at the electrode surface may be given as:

$$d^2d^0d^0\left[D^2SP^3\right] \xrightarrow{-e} d^1d^0d^0\left[D^2SP^3\right] \xrightarrow{-e} d^0d^0d^0\ \left[D^2SP^3\right]$$

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C H A P T E R - II:

Acid Dissociation Constants of Tripotassium oxo-hydroxotetracyanomolybdate(IV) and Tetrapotassium Dioxo-tetracyanotungstate(IV).

Litvinchuk and Mikhalevich[1] determined the acid dissociation constants of hydroxocyanides of Mo and W from hydrolysis studies. For pH measurements the following galvanic cell was assembled.

$$Hg^{+}\left|HgO\right|KOH\left|KCl\right|K_n\left[M(OH)_n(H_2O)_{4-n}(CN)_4\right]\left|Pt^{-}\right.$$

The potential of the reference of electrode is given as

$$E_{ref.} = E_{obs.} + \frac{RT}{F}\ln K^{+} + \text{constant} \qquad \ldots\ldots \quad (1)$$

For two concentrations of the potassium salt, two different values of $E_{obs.}$ will be obtained. Thus, by forming two equations of the type of relation(1), one may calculate the concentration of K^{+}. Based on the ionic power of the solution, the value of activity coefficients(f) of the OH^{-} ions was found out. Then the hydroxyl ion concentration was calculated (h%) by the formulae:

$$K'_{H_2O} = \left[aOH^{-}\right] \cdot \left[aH^{+}\right] \; ; \; C_{OH^{-}} = \frac{aOH^{-}}{f} \qquad h\% = \frac{C_{OH^{-}} \cdot 100}{C_{MeR}} \qquad \ldots\ldots \quad (2)$$

As Nadenski[2] shows, the determination of the hydrolysis constant from the values of $K'_{H_2O}, C_{OH^{-}}, C_{MeR}$, on the law of mass action.

$$K_{Hydrolysis} = \frac{\left[OH^{-}\right]^2 - K'_{H_2O}/f^2}{C_{MeR} - \left[OH^{-}\right]} \qquad \ldots\ldots \quad (3)$$

Using the hydrolysis constant, the dissociation constant of the complex acid was calculated by a corresponding step:

$$K_{HR} = \frac{K'_{H_2O}}{K_{Hydrolysis}} \qquad \ldots\ldots\ldots \quad (4)$$

Measurements were made for doubly-, triply-, and four times-substituted hydroxocyanides of both molybdenum and tungsten at 16°C. The average values of K_4, K_3 and K_2 for Mo are respectively 2.2×10^{-13}, 1.8×10^{-9}, 7.9×10^{-7} and for W 1.2×10^{-11}, 2.9×10^{-8} and 7.9×10^{-6}

Litvinchuk and Mikhalevich reported measurements of hydrolysis constants at 16°C for reactions of the type.

$$\left[Mo(OH)_4(CN)_4\right]^{4-} + H_2O \rightleftharpoons \left[Mo(OH)_3(H_2O)(CN)_4\right]^{3-} + OH^-$$

This is now be formulates as

$$\left[MoO_2(CN)_4\right]^{4-} + H_2O \rightleftharpoons \left[Mo(OH)(CN)_4\right]^{3-} + OH^-$$

Their values result from measurements of the pH of solutions of the appropriate salts. Although this method is satisfactory in principle, its success is dependent on using a salt quite free of the conjugate acid or conjugate base of the an ion whose hydrolysis is being measured. This would be easy with $K_4\left[MoO_2(CN)_4\right]$, difficult with $K_3\left[MoO(OH)(CN)_4\right]$, and very difficult with $K_2\left[Mo(OH)_2(CN)_4\right]$. The pH's they report for solutions of $K_2\left[Mo(OH)_2(H_2O)_2(CN)_4\right]$ are more basic than those observed with $K_2\left[Mo(OH)_2(CN)_4\right]$ although these must be single

compound. Their value for the acid dissociation constant of $[MoO(OH)(CN)_4]^{3-}$, calculated from the hydrolysis of $[MoO_2(CN)_4]^{4-}$, is meaningful, but the other two constants are probably not.

Potentiometric titrations may frequently used as convenient and accurate methods of analysis. The methods are also of service in determining ionization constants, and solubilities of slightly soluble substances. A decided advantage of potentiometric titrations over the usual indicator methods is that the progress of titration may be followed from beginning to end, whereas, the general, indicators are of service in deciding upon the end points only.

The fundamental reason for the utility of the potentiometric method in acid-base titrations may be seen from the equation (1).

$$E = E^0 - \frac{RT}{nF} \log \frac{a_{H^+}}{pH^2}$$

Where one of the electrode is the hydrogen electrode. If the pressure of hydrogen is one atmosphere, the above reduces to

$$E = E^0 + \frac{RT}{F} pH \qquad \ldots\ldots \quad (1)$$

For the purpose of the following rough computation the pH of the strong acid, HA, may be considered to be

$$pH = - \log C_{H^+} \qquad \ldots\ldots \quad (2)$$

Equation (1) thus becomes,

$$E = E^{o} - \frac{RT}{F} \log C_{H^{+}} \qquad \ldots\ldots (3)$$

The values of ionization constants of weak acids and weak bases can be estimated by means of potentiometric titration. Since the ionization constant K of a weak acid H_A is given by

$$K = \frac{(a_{H^{+}})(a_{A^{-}})}{(a_{HA})}$$

Whereas $a_{H^{+}}$ and $a_{A^{-}}$ are the activities.

This may, within the limitations of pH measurements, be put into the form

$$pK = pH - \log\frac{(a_{A^{-}})}{(a_{HA})} = pH - \log\frac{[C_{A^{-}}]}{[C_{HA}]} - \log f \qquad \ldots\ldots (4)$$

Here $pK = -\log K$, and f is the ratio of activity coefficient. If we define

$$pK' = pK + \log f \qquad \ldots\ldots\ldots (5)$$

then equation (4) becomes

$$pK' = pH - \log\frac{[A^{-}]}{[HA]}$$

Thus the pK' value is equal to pH when the ratio of the free acid to salt is unity, i.e., the titration is half completed.

The corresponding equation for a weak base may be readily seen to be

$$pK_w - pK'_B = pH + \log \frac{[B^+]}{[B]} \qquad \ldots\ldots \quad (6)$$

Titration of free acid by alkali is usually carried out with the aim of establishing the basicity of the acid and examining the possibility of formation of different types of salts. In our investigations, because of the instability of the complex acids, we carried out titrations of the potassium salts of hydroxocyanides by 0.1M hydrochloric acid. The acid dissociation constants of TCM and TCT have been determined for a wide range of temperature and ionic strength.

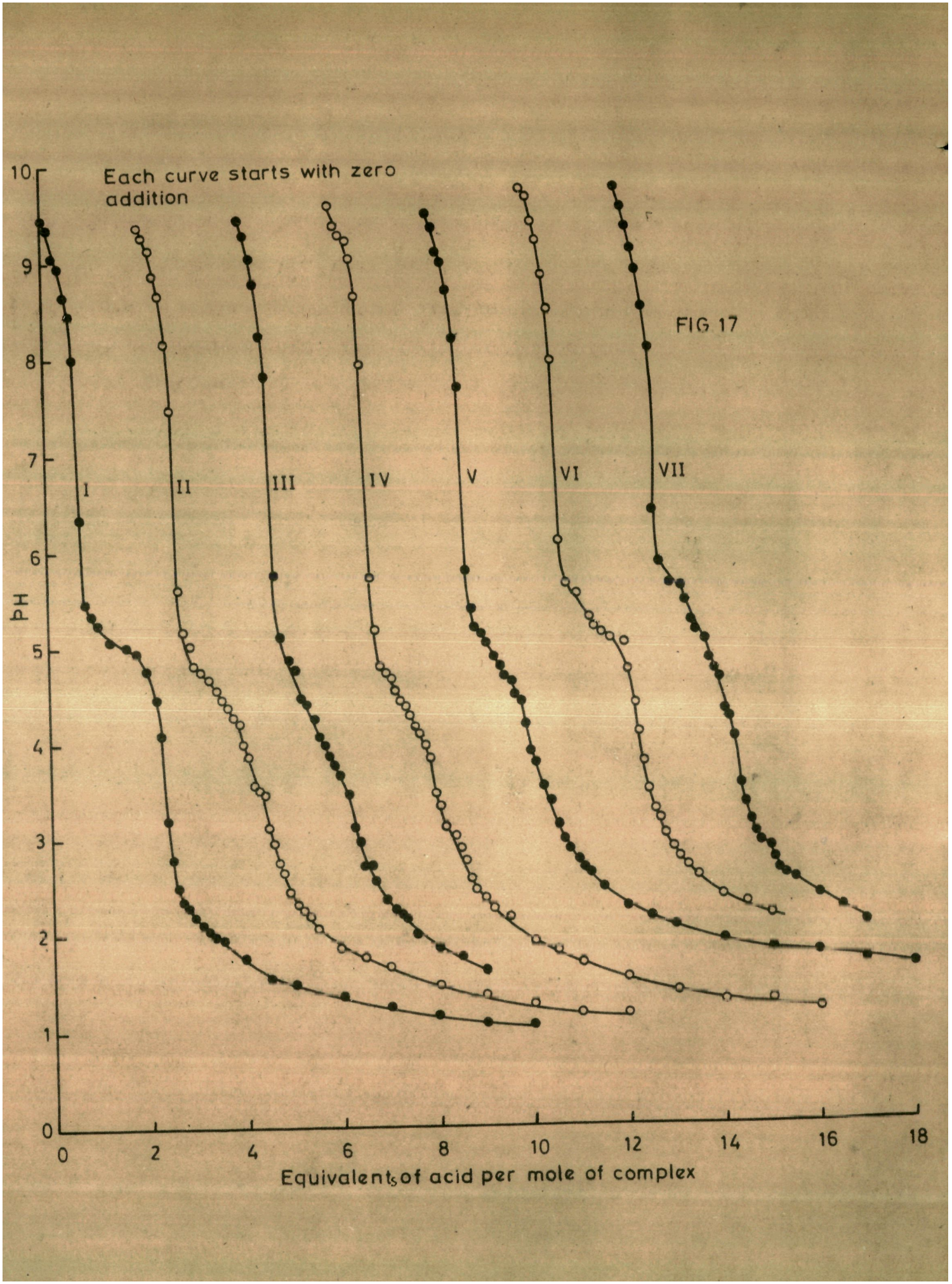
EXPERIMENTAL

Solutions of blue $K_3[MoO(OH)(CN)_4]$ (TCM) and Violet $K_4[WO_2(CN)_4]$ (TCT) were prepared and their strength were determined as reported earlier (Chapter I).

Reagent grade chemicals were used throughout. Doubly distilled water served as the solvent. To obviate air oxidation, experiments were carried out in a nitrogen atmosphere. Nitrogen was purified and equilibrated with the solvent.

(A) Determination of dissociation constants:

The acid dissociation constants were determined from acidimetric titration curves. Aqueous solutions of TCM/TCT were titrated with 0.1M aqueous hydrochloric acid and the concomitant change in the pH was read with a Beckman G/ELICO LI-12 pH-meter using glass (Beckman 40485/Type EM-60) and calomel (Beckman 39970/ELICO) electrodes. The pH-meter was calibrated with reference to a 0.05M potassium hydrogen phthalate aqueous solution, whose pH value is known at several temperatures.[3] Ionic strengths were maintained by adding appropriate concentrations of potassium chloride. The equilibrium constants pK_3' and pK_2' were obtained from the half equivalence points of the respective segments. To


Each curve starts with zero addition
FIG 17
I
II
III
IV
V
VI
VII
pH
10
9
8
7
6
5
4
3
2
1
0
0
2
4
6
8
10
12
14
16
18
Equivalents of acid per mole of complex

determine the effect of temperature on the dissociation constant, titrations were done at several temperatures. Further, to calculate the standard values of the thermodynamic functions, each titration was done at several ionic strengths.

The following tables record the observations:

T A B L E -17

Vol.of TCM = 35.0 ml
Concn.of TCM = 0.002M
Concn.of HCl = 0.1M
Temperature = 25°C

Vol.of HCl added (ml.)	pH						
	Ionic Strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
0.0	0.45	9.35	9.55	9.55	9.45	9.70	9.70
0.1	9.35	9.25	9.40	9.35	9.30	9.60	9.50
0.2	9.05	9.10	9.25	9.25	9.05	9.35	9.30
0.3	8.95	8.85	9.00	9.20	8.95	9.15	9.05
0.4	8.65	8.65	8.75	9.00	8.65	8.80	8.85
0.5	8.45	8.15	8.70	8.60	8.15	8.45	8.45
0.6	8.00	7.45	7.80	7.90	7.65	8.90	8.05
0.7	6.35	5.60	5.75	5.70	5.75	6.05	6.35
0.8	5.45	5.15	5.10	5.15	5.35	5.60	5.80
0.9	5.35	5.00	-	4.75	5.15	•	•
1.0	5.25	4.80	4.85	4.70	5.10	5.50	5.60
1.1	5.25	4.75	4.75	4.65	5.00	5.50	5.55

(Contd.)

T A B L E -17(Contd.)

1.2	5.05	4.75	4.45	4.50	5.00	-	5.55
1.3	5.05	4.65	4.40	4.40	4.85	5.25	5.40
1.4	-	4.55	4.25	4.35	4.75	5.15	5.20
1.5	-	4.55	4.25	4.25	4.65	5.10	5.10
1.6	5.00	4.45	4.05	4.15	4.60	5.10	5.10
1.7	-	4.35	3.95	4.05	4.45	5.05	5.00
1.8	4.95	4.25	3.85	3.95	4.40	5.00	4.80
1.9	4.75	4.20	3.75	3.80	4.15	-	4.70
2.0	4.75	3.95	3.65	3.45	3.85	5.0	4.60
2.1	4.50	3.85	3.65	3.30	3.75	4.75	4.30
2.2	4.45	3.55	3.45	3.10	-	4.35	4.20
2.3	4.10	3.50	3.10	3.05	3.50	4.05	4.00
2.4	3.20	3.20	2.95	3.00	3.35	3.75	3.50
2.5	2.80	3.10	2.70	2.85	3.35	3.45	3.30
2.6	2.50	2.95	2.70	2.75	3.10	3.25	3.10
2.7	2.35	2.75	2.55	2.55	2.95	3.15	3.00
2.8	2.30	2.65	2.55	2.45	2.85	3.00	2.90
2.9	2.20	2.45	2.35	2.45	2.75	2.95	2.85
3.0	2.15	2.45	2.35	2.35	2.75	2.85	2.85
3.1	2.10	2.30	2.25	2.30	2.65	2.75	2.75
3.2	2.05	2.25	2.20	2.25	2.60	2.70	2.60
3.3	2.00	2.20	2.15	2.25	2.55	2.65	2.55
3.5	1.95	2.05	2.00	2.15	2.45	2.55	2.50
4.0	1.75	1.85	1.85	1.90	2.25	2.35	2.35
4.5	1.55	1.75	1.75	1.80	2.15	2.25	2.20
5.0	1.50	1.65	1.60	1.65	2.05	2.15	2.05
6.0	1.35	1.45	-	1.50	1.90	-	-
7.0	1.25	1.35	-	1.35	1.85	-	-
8.0	1.15	1.25	-	1.25	1.75	-	-
9.0	1.05	1.15	-	1.25	1.65	-	-
10.0	1.05	1.15	-	1.15	1.60	-	-

Fig.(17)Curve(I)Curve(II)Curve(III)Curve(IV)Curve(VI Curve(VI)Curve(VII)

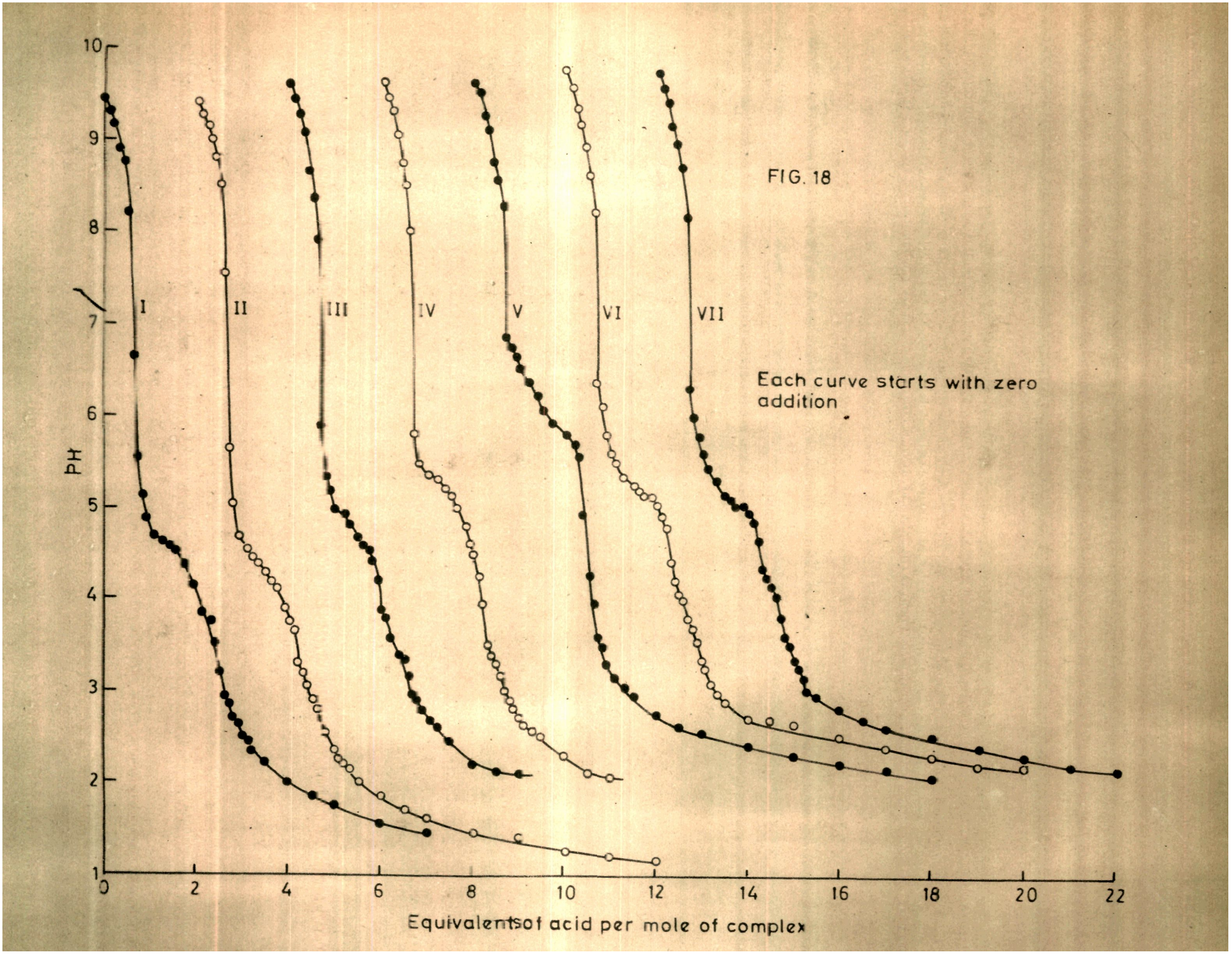


FIG. 18
Each curve starts with zero addition
I
II
III
IV
V
VI
VII
PH
Equivalentsof acid per mole of complex
10
9
8
7
6
5
4
3
2
1
0
2
4
6
8
10
12
14
16
18
20
22

T A B L E -18.

Vol.of TCM = 35.0 ml.
Concn.of TCM = 0.002 M
Concn.of HCl = 0.1M
Temperature = 30°C

Vol.of HCl added (ml.)	pH						
	Ionic Strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
0.0	9.45	9.40	9.60	9.60	9.60	9.75	9.75
0.1	9.30	9.25	9.45	9.45	9.50	9.55	9.55
0.2	9.15	9.15	9.25	9.30	9.25	9.35	9.40
0.3	8.90	9.00	9.05	9.05	9.10	9.15	9.15
0.4	8.75	8.80	8.65	8.75	8.75	8.90	8.95
0.5	8.20	8.50	8.35	8.50	8.55	8.60	8.75
0.6	6.65	7.55	7.90	8.00	8.25	8.20	8.15
0.7	5.55	5.65	5.90	5.80	6.85	6.35	6.30
0.8	5.15	5.05	5.35	5.50	6.75	6.10	6.00
0.9	4.90	4.70	5.20	5.45	6.60	5.80	5.80
1.0	4.85	4.55	5.00	5.35	6.50	5.60	5.60
1.1	4.70	4.55	-	-	6.50	5.50	5.45
1.2	4.65	4.45	4.95	5.35	6.35	-	-
1.3	4.65	4.40	4.85	-	6.35	5.35	5.30
1.4	4.60	4.35	4.70	5.20	6.25	-	-
1.5	4.55	4.30	4.70	5.15	6.05	5.25	5.15
1.6	4.35	4.20	4.60	5.00	6.05	5.20	5.10
1.7	4.35	4.15	4.55	5.00	5.90	5.15	5.05
1.8	4.35	3.95	4.40	4.80	5.90	-	-
1.9	4.15	3.90	4.20	4.60	5.90	5.15	5.05

(Contd.)

T A B L E -18.(Contd.)-

2.0	4.15	3.75	3.90	4.50	5.80	5.05	4.95
2.1	3.85	3.65	3.80	4.25	5.75	4.90	4.85
2.2	3.85	3.30	3.55	3.95	5.70	4.80	4.65
2.3	2.75	3.20	-	3.50	5.55	4.40	4.35
2.4	3.50	3.05	3.40	3.40	4.95	4.20	4.25
2.5	3.20	2.90	3.35	3.30	4.25	4.05	4.15
2.6	2.95	2.80	3.15	3.15	3.95	4.00	4.05
2.7	2.85	2.55	2.95	3.00	3.60	3.80	3.50
2.8	2.70	2.55	2.90	2.90	3.50	3.70	3.60
2.9	2.65	2.35	2.80	2.80	3.30	3.55	3.50
3.0	2.50	2.35	2.80	2.70	3.25	3.35	3.35
3.1	2.45	2.25	2.65	2.65	3.15	3.25	3.25
3.2	2.35	2.20	2.60	-	3.10	3.10	3.15
3.3	2.30	2.15	2.60	2.55	3.05	3.00	3.00
3.5	2.20	2.00	2.45	2.50	2.95	2.90	2.95
4.0	2.00	1.85	2.20	2.30	2.75	2.70	2.80
4.5	1.85	1.70	2.10	2.10	2.60	2.70	2.70
5.0	1.75	1.60	2.10	2.05	2.55	2.65	2.60
6.0	1.55	1.45	-	-	2.40	2.50	2.50
7.0	1.45	1.40	-	-	2.30	2.40	2.40
8.0	-	1.25	-	-	2.20	2.30	2.30
9.0	-	1.20	-	-	2.15	2.20	2.20
10.0	-	1.15	-	-	2.05	2.20	2.15

Fig.(18)Curve(I)Curve(II)Curve(III)Curve(IV)Curve(V)Curve(VI)Curve(VII)

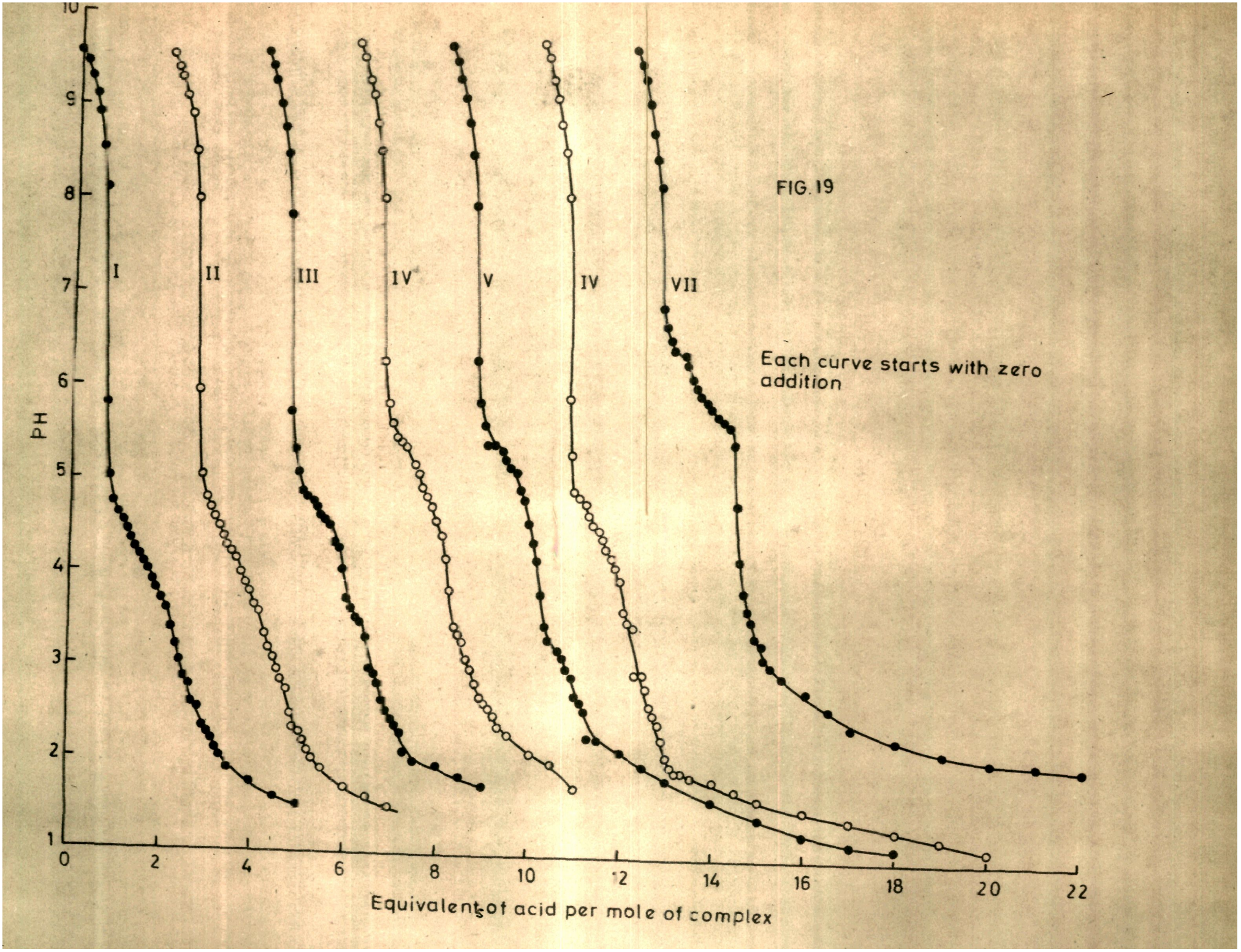


FIG. 19
Each curve starts with zero addition
I
II
III
IV
V
IV
VII
pH
Equivalents of acid per mole of complex
0
2
4
6
8
10
12
14
16
18
20
22
1
2
3
4
5
6
7
8
9
10

TABLE - 19.

Vol. of TCM = 35.0 ml
Concn. of TCM = 0.002M
Concn. of HCl = 0.1M
Temperature = 35°C

Vol. of HCl added (ml.)	pH						
	Ionic Strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
0.0	9.55	9.55	9.60	9.70	9.70	9.75	9.70
0.1	9.45	9.40	9.45	9.55	9.55	9.60	9.55
0.2	9.30	9.30	9.30	9.30	9.35	9.35	9.40
0.3	9.10	9.10	9.05	9.15	9.10	9.15	9.15
0.4	8.90	8.90	8.80	8.85	8.90	8.90	8.80
0.5	8.55	8.50	8.50	8.55	8.55	8.60	8.55
0.6	8.10	8.00	7.85	8.05	8.00	8.10	8.25
0.7	5.85	5.95	5.75	6.30	6.35	5.95	6.95
0.8	5.00	5.05	5.35	5.85	5.90	5.35	6.75
0.9	4.75	4.80	5.10	5.65	5.65	4.95	6.60
1.0	4.65	4.70	4.90	5.50	5.45	4.90	6.50
1.1	4.55	4.60	4.85	5.45	5.45	4.85	6.50
1.2	4.45	4.50	4.80	5.40	5.45	4.70	6.45
1.3	4.35	4.40	4.75	-	5.40	4.60	6.35
1.4	4.25	4.30	4.65	5.20	5.30	4.55	6.20
1.5	4.20	4.25	4.60	5.10	5.20	4.45	6.10

(Contd.)

T A B L E -19.(Contd.)

1.6	4.10	4.15	4.55	4.95	5.15	4.35	6.00
1.7	4.05	4.00	4.35	4.85	4.95	4.25	5.95
1.8	3.90	3.90	4.30	4.75	4.85	4.15	5.90
1.9	3.80	3.80	4.05	4.60	4.60	4.00	5.85
2.0	3.70	3.65	3.75	4.45	4.40	3.65	5.80
2.1	3.60	3.60	3.65	4.20	4.20	3.55	5.75
2.2	3.40	3.35	3.55	3.85	3.85	3.25	5.70
2.3	3.20	3.20	3.50	3.45	3.50	3.00	5.50
2.4	3.05	3.10	3.35	3.40	3.35	3.00	4.85
2.5	2.85	2.95	3.00	3.30	3.30	2.85	4.25
2.5	2.80	2.85	2.95	3.10	3.25	2.65	3.90
2.6	2.80	2.85	2.95	3.10	3.25	2.65	3.90
2.7	2.60	2.75	2.85	3.00	3.15	2.55	3.70
2.8	2.55	2.50	2.65	2.85	3.05	2.45	3.60
2.9	2.35	2.35	2.55	2.70	2.95	2.30	3.40
3.0	2.30	2.30	2.45	2.65	2.75	2.10	3.35
3.1	2.20	2.20	2.40	2.60	2.70	2.00	3.20
3.2	2.10	2.10	2.30	2.50	2.60	1.95	3.10
3.3	2.05	2.00	2.10	2.40	2.30	1.95	-
3.5	1.90	1.90	2.00	2.30	2.30	1.90	3.00
4.0	1.75	1.70	1.95	2.10	2.15	1.85	2.85

(Contd.)

T A B L E -19.(Contd.)

4.5	1.60	1.60	1.85	2.00	2.00	1.75	2.65
5.0	1.50	1.50	1.75	1.75	1.85	1.65	2.45
6.0	-	-	-	-	1.65	1.55	2.35
7.0	-	-	-	-	1.45	1.45	2.20
8.0	-	-	-	-	1.30	1.35	2.10
9.0	-	-	-	-	1.20	1.25	2.10
10.0	-	-	-	-	1.15	1.15	2.05

Fig.19 (Curve(I)Curve(II)Curve(III)Curve(IV)Curve(V)Curve(VI)Curve(VI:

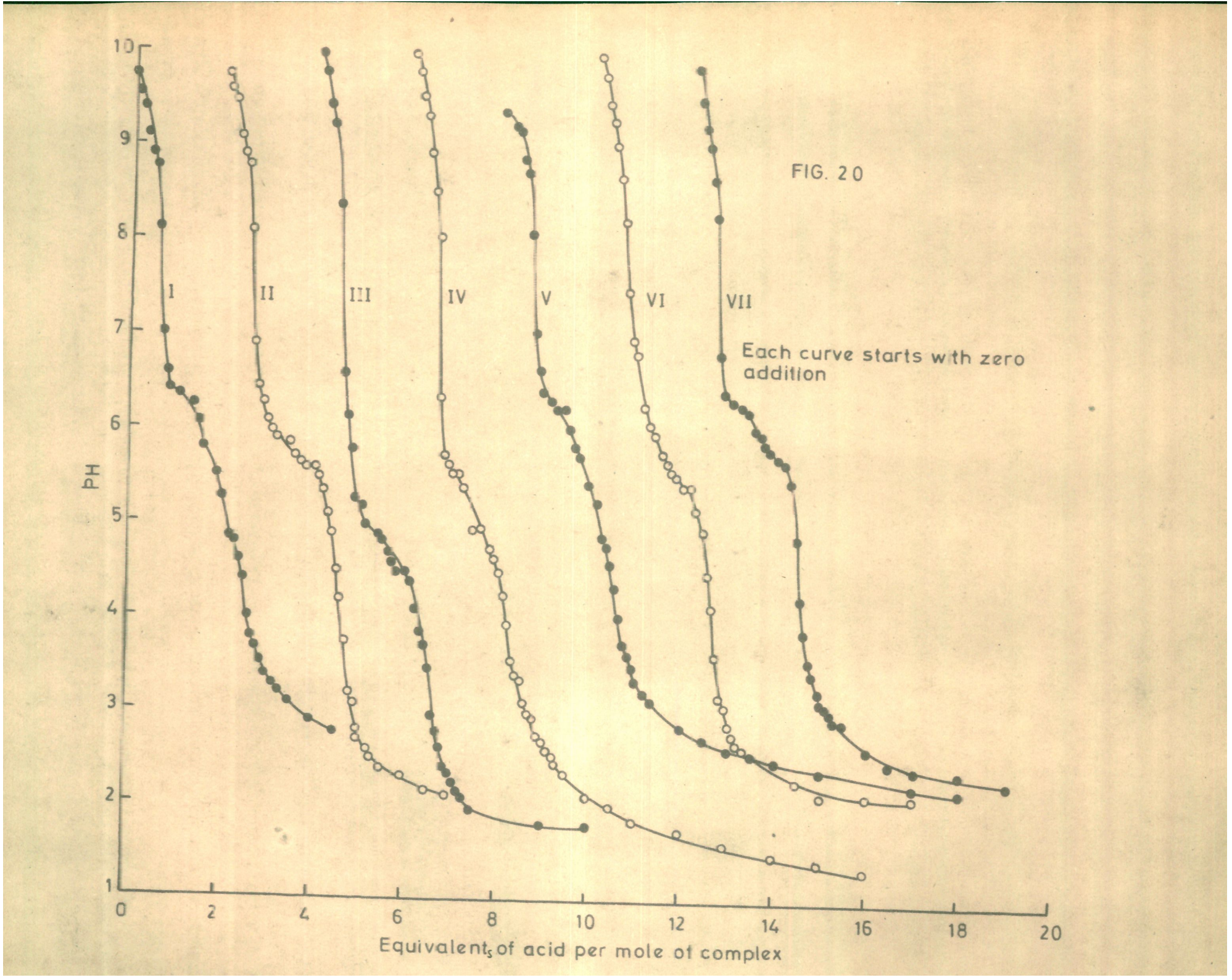


FIG. 20
pH
Equivalents of acid per mole of complex
I
II
III
IV
V
VI
VII
Each curve starts with zero addition
10
9
8
7
6
5
4
3
2
1
0
2
4
6
8
10
12
14
16
18
20

TABLE -20.

Vol. of TCM = 35.0 ml.
Concn. of TCM = 0.002M
Concn. of HCl = 0.1M
Temperature = 40°C

Vol. of HCl added (ml.)	pH						
	Ionic Strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
0.0	9.75	9.75	10.00	10.00	9.40	10.00	10.05
0.1	9.55	9.60	9.80	9.80	-	9.80	9.90
0.2	9.40	9.50	9.45	9.55	9.25	9.50	9.55
0.3	9.10	9.10	9.25	9.35	9.20	9.30	9.25
0.4	8.90	8.90	9.95	8.95	8.90	9.05	9.05
0.5	8.75	8.80	8.40	8.55	8.75	8.70	8.70
0.6	8.10	8.10	6.60	8.05	8.10	8.25	8.30
0.7	8.00	6.90	6.15	6.35	7.05	7.50	6.80
0.8	6.60	6.45	5.80	5.75	6.65	7.00	6.45
0.9	6.40	6.30	5.25	5.65	6.45	6.85	6.45
1.0	6.40	6.10	5.20	5.55	-	-	6.35
1.1	6.35	6.00	5.00	5.55	6.35	6.30	-

(Contd.)

TABLE -20(Contd.)

1.2	6.25	5.90	5.00	5.40	6.25	6.10	6.30
1.3	-	-	-	-	-	6.00	6.25
1.4	6.25	-	4.90	4.95	6.25	6.00	-
1.5	6.05	5.85	4.85	-	6.05	5.80	6.05
1.6	5.80	5.70	4.70	4.95	5.85	5.70	6.00
1.7	5.75	5.65	4.60	-	5.75	5.60	5.90
1.8	-	5.60	4.50	4.75	-	5.55	5.85
1.9	5.50	5.60	-	4.65	5.45	5.55	-
2.0	5.25	5.60	4.50	4.50	-	5.45	5.75
2.1	-	5.50	4.40	4.25	5.25	5.45	5.70
2.2	4.85	5.35	4.10	3.95	4.90	5.20	5.65
2.3	4.80	5.10	3.85	3.55	4.80	5.20	5.50
2.4	4.60	4.90	3.70	3.40	4.60	4.95	4.90
2.5	4.40	4.50	3.45	3.35	4.35	4.50	4.25
2.6	4.00	4.20	2.95	3.10	4.05	4.15	3.90
2.7	3.80	3.75	2.80	3.00	3.75	3.65	3.60
2.8	3.70	3.20	2.60	2.95	3.65	3.20	3.45
2.9	3.55	3.10	3.40	2.75	3.50	3.10	3.25
3.0	3.40	2.80	2.35	2.70	3.35	2.90	3.15

(Contd.)

TABLE - 20.

3.1	3.40	2.70	2.25	2.60	3.35	2.80	3.10
3.2	3.30	2.60	2.15	2.55	3.25	2.70	3.05
3.3	3.20	2.50	2.10	2.45	3.15	2.65	2.95
3.5	3.10	2.40	1.95	2.35	3.05	2.60	2.95
4.0	2.90	2.30	-	2.10	2.85	2.50	2.65
4.5	2.80	2.15	-	2.00	2.75	2.30	2.50
5.0	2.70	2.10	1.8	1.85	2.65	2.15	2.45
6.0	-	-	1.8	1.75	2.50	2.15	2.40
7.0	-	-	-	1.60	2.40	2.15	2.30
8.0	-	-	-	1.50	2.35	-	-
9.0	-	-	-	1.45	2.25	-	-
10.0	-	-	-	1.35	2.20	-	-

Fig.(20) Curve(I) Curve(II)Curve(III)Curve(IV)Curve(V)Curve(VI)Curve(VII)

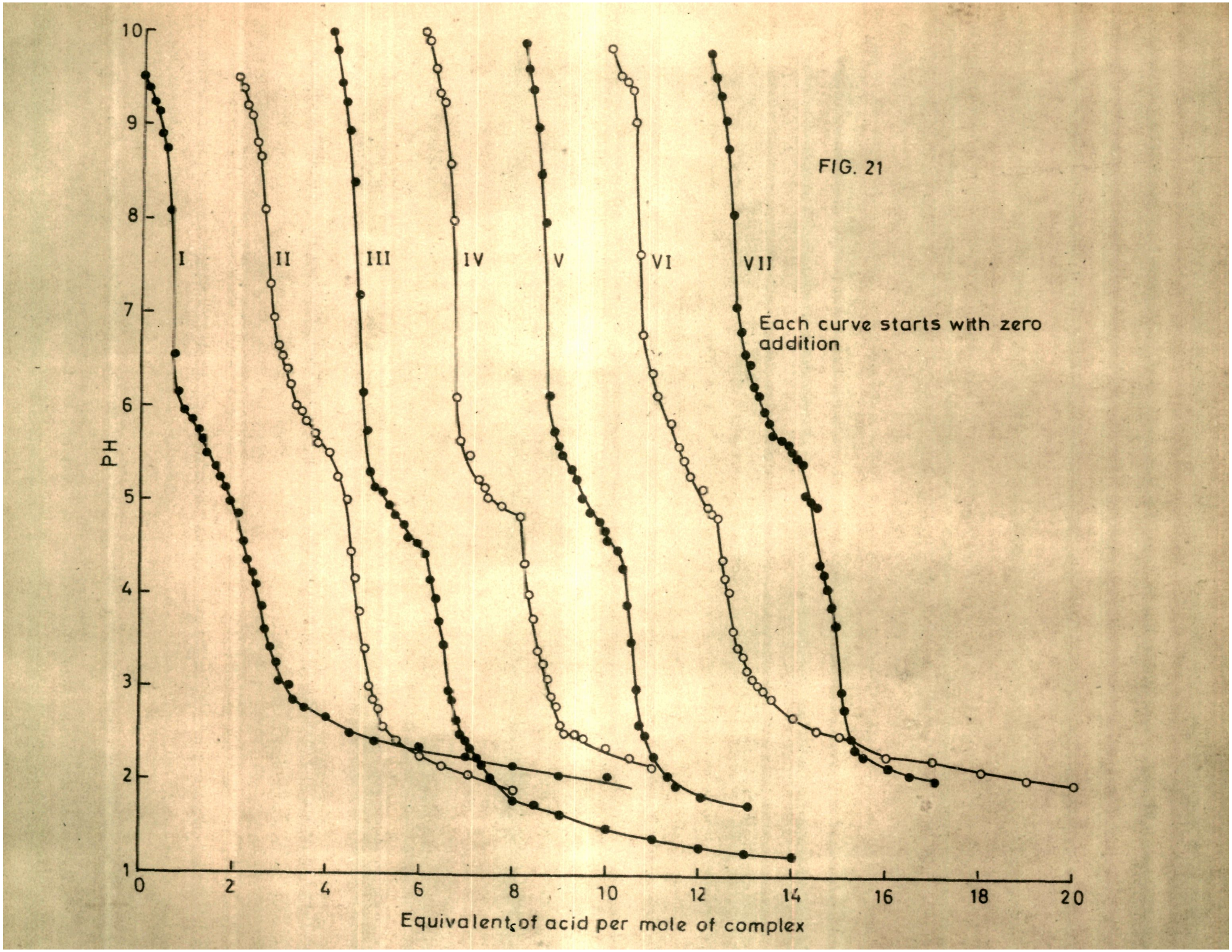


FIG. 21
I
II
III
IV
V
VI
VII
Each curve starts with zero addition
PH
Equivalents of acid per mole of complex
10
9
8
7
6
5
4
3
2
1
0
2
4
6
8
10
12
14
16
18
20

T A B L E - 21.

Vol. of TCM = 35.0 ml.
Concn. of TCM = 0.002M
Concn. of HCl = 0.1N
Temperature = 45°C

Vol. of HCl added (ml.)	pH						
	Ionic Strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
0.0	9.50	9.50	10.00	10.00	10.05	9.85	10.05
0.1	9.40	9.40	9.80	9.90	9.90	-	9.80
0.2	9.25	9.20	9.45	9.60	9.60	9.55	9.55
0.3	9.15	9.10	9.25	9.35	9.40	9.25	9.35
0.4	8.90	8.80	8.95	9.00	9.00	8.90	9.10
0.5	8.75	8.65	8.40	8.60	8.50	8.55	8.80
0.6	8.10	8.10	7.20	8.00	8.00	7.65	8.10
0.7	6.55	7.30	6.15	6.10	6.15	6.80	7.15
0.8	6.15	6.95	5.75	5.65	5.75	6.25	6.85
0.9	5.95	6.65	5.30	5.60	5.60	6.40	6.60
1.0	-	6.55	5.15	5.50	5.50	6.15	6.50
1.1	5.85	6.40	5.10	5.50	5.50	5.90	6.25
1.2	5.75	6.25	5.05	5.25	5.35	-	6.15

(Contd.)

T A B L E -21.(Contd.)

1.3	5.65	6.00	4.95	5.15	5.25	5.85	6.00
1.4	5.50	5.95	4.85	5.05	5.05	-	5.85
1.5	-	5.85	4.85	5.00	5.05	5.60	5.75
1.6	5.35	5.80	4.75	-	4.90	5.45	5.70
1.7	5.25	5.70	4.60	4.95	4.90	5.30	5.70
1.8	5.15	5.60	4.55	-	4.80	-	5.65
1.9	5.00	5.60	4.55	-	4.70	5.30	5.55
2.0	-	5.50	4.55	-	4.60	5.15	5.50
2.1	4.85	-	4.45	4.85	4.55	4.95	5.45
2.2	4.55	5.25	4.15	4.35	4.50	4.90	5.10
2.3	4.35	5.25	3.95	4.00	4.30	4.85	5.05
2.4	4.20	5.00	3.70	3.75	3.80	4.40	5.00
2.5	4.10	4.45	3.45	3.40	3.50	4.20	4.35
2.6	3.85	4.15	2.95	3.25	3.00	4.05	4.25
2.7	3.55	3.80	2.85	3.10	2.60	3.65	4.10
2.8	3.40	3.40	2.65	2.90	2.50	3.45	3.90
2.9	2.25	3.00	2.50	2.80	2.30	3.35	3.70
3.0	3.05	2.85	2.45	2.60	2.25	3.20	3.00
3.1	3.05	2.75	2.35	2.50	2.15	3.10	2.80

(Contd.)

T A B L E -21.(Contd.)

3.2	3.00	2.55	2.25	-	-	3.05	2.50
3.3	2.85	2.50	2.20	2.50	2.05	3.0	2.40
3.5	2.75	2.40	2.05	2.45	1.95	2.90	2.30
4.0	2.65	2.30	1.85	2.35	1.85	2.70	2.20
4.5	2.50	2.15	1.75	2.25	-	2.55	2.10
5.0	2.40	2.05	1.65	2.15	1.75	2.50	2.05
6.0	2.35	1.90	1.50	-	-	2.30	-
7.0	2.20	-	1.40	-	-	2.25	-
8.0	2.15	-	1.30	-	-	2.15	-
9.0	2.05	-	1.25	-	-	2.05	-
10.0	2.05	-	1.20	-	-	2.00	-

Fig.21 Curve(I) Curve(II) Curve(III) Curve(IV) Curve(V) Curve(VI) Curve(VII)

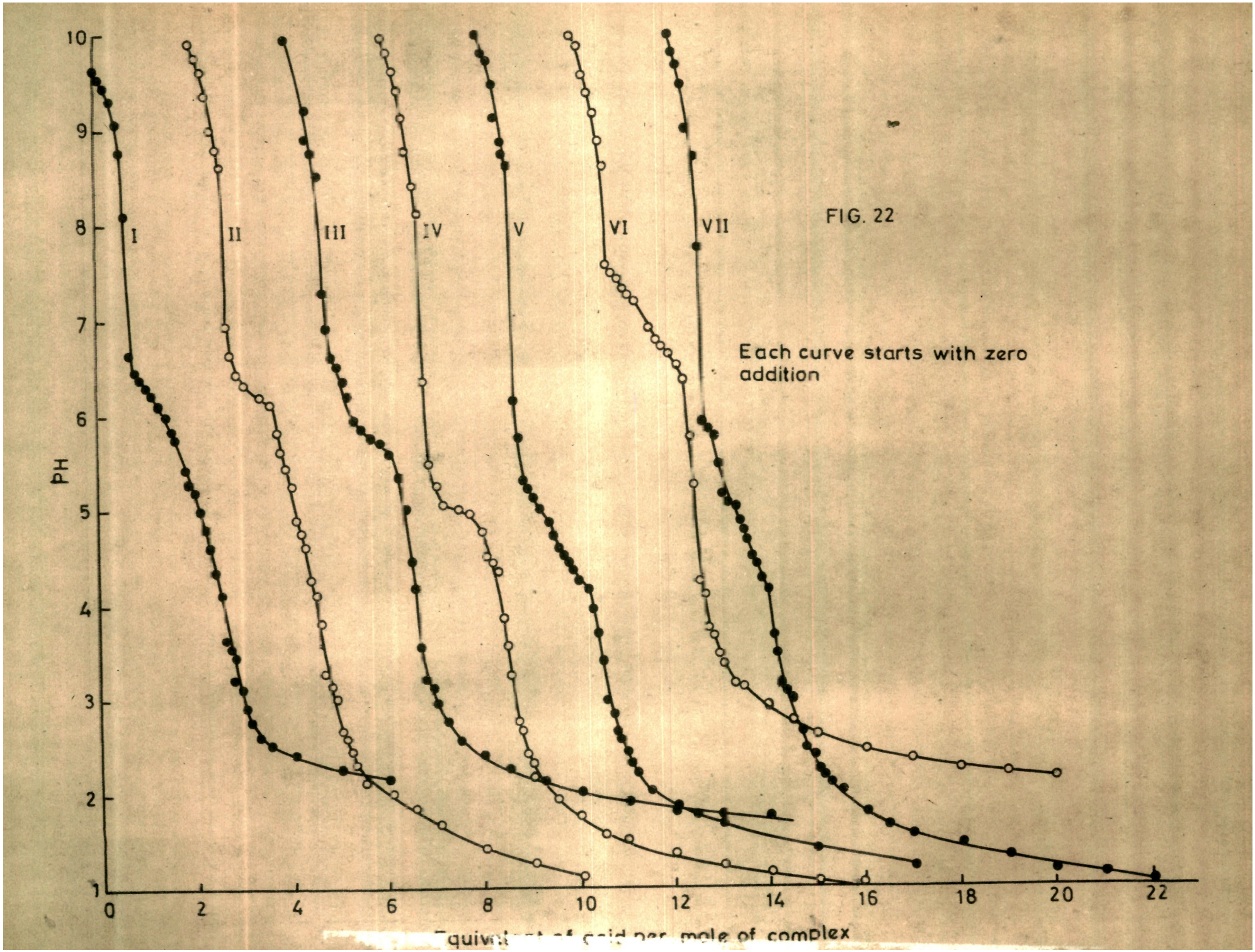

PH
10
9
8
7
6
5
4
3
2
1
0
2
4
6
8
10
12
14
16
18
20
22
I
II
III
IV
V
VI
VII
Each curve starts with zero addition
Equivalent of acid per mole of complex

FIG. 22

TABLE-22.

Vol. of TCM = 35.0 ml.
Concn. of TCM = 0.002M
Concn. of HCl = 0.1M
Temperature = 50°C

Vol. of HCl added (ml.)	pH						
	Ionic Strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
0.0	9.65	9.90	9.95	9.95	10.0	9.95	10.0
0.1	9.55	9.75	-	9.80	9.80	9.85	9.80
0.2	9.45	9.60	-	9.60	9.70	9.55	9.65
0.3	9.30	9.35	-	9.40	9.45	9.35	9.45
0.35	-	-	9.20	-	-	-	-
0.4	9.05	9.0	8.90	9.10	9.10	9.15	9.0
0.5	8.75	8.80	8.75	8.75	8.75	8.85	8.70
0.6	8.10	8.60	8.0	8.40	8.10	8.60	7.75
0.7	6.65	6.90	7.30	8.10	6.15	7.55	5.90
0.8	6.45	6.65	6.90	6.35	5.75	7.45	5.85
0.9	6.40	6.45	6.60	5.45	5.30	7.40	5.75
1.0	6.30	6.30	6.50	5.25	5.20	7.30	5.45
1.1	6.20	6.30	6.35	5.25	5.10	7.25	5.10

(Contd.)

T A B L E -22.(Contd.)

1.2	6.10	6.25	6.20	5.05	5.00	7.20	5.05
1.3	6.05	-	5.95	-	-	-	5.05
1.4	6.00	6.20	-	-	4.85	-	4.85
1.5	5.85	-	5.85	-	4.70	-	4.75
1.6	5.75	6.10	5.80	5.0	4.60	6.9	4.65
1.7	5.45	5.85	5.75	-	4.50	6.75	4.45
1.8	5.45	5.65	-	4.95	4.45	6.70	4.40
1.9	5.25	5.45	5.70	4.75	4.35	6.65	4.25
2.0	5.20	5.25	5.60	4.75	4.25	6.60	4.15
2.1	5.00	4.90	5.60	4.5	4.25	6.50	3.65
2.2	4.80	4.75	5.35	4.45	4.15	6.35	3.45
2.3	4.60	4.60	5.35	4.10	3.95	6.35	3.15
2.4	4.35	4.25	5.0	3.85	3.70	5.75	3.05
2.5	4.10	4.10	4.45	3.55	3.40	5.25	2.95
2.6	3.65	3.80	4.15	3.25	3.0	4.25	2.70
2.7	3.55	3.25	3.55	2.75	2.85	4.10	2.65
2.8	3.20	3.10	3.20	2.65	2.65	3.75	2.45
2.9	3.10	3.00	3.10	2.40	2.55	3.65	2.40
3.0	2.90	2.65	2.95	2.30	2.45	3.45	2.25
3.1	2.75	2.55	2.85	2.15	2.30	3.35	2.25

(Contd.)

T A B L E -22.(Contd.)

3.2	-	2.45	2.75	2.10	2.20	2.25	2.25
3.3	2.60	2.30	2.70	2.00	2.15	3.15	2.10
3.5	2.50	2.10	2.55	1.95	2.00	3.10	2.0
4.0	2.40	2.00	2.40	1.75	1.85	2.90	1.80
4.5	-	1.85	2.25	1.55	1.75	2.75	1.65
5.0	2.25	1.65	2.15	1.50	1.65	2.60	1.55
6.0	2.15	1.40	2.0	1.35	-	2.45	1.45
7.0	-	1.25	1.90	1.25	1.40	2.35	1.30
8.0	-	1.10	1.80	1.15	-	2.25	1.15
9.0	-	-	1.75	1.05	-	2.20	1.15
10.0	-	-	1.75	1.05	1.20	2.15	1.05

Fig.(22)Curve(I)Curve(II)Curve(III)Curve(IV)Curve(V)Curve(VI)Curve(VII))

DISCUSSION

The potentiometric titrations of TCM(IV) with hydrochloric acid show two inflection points. The first inflection lying at a pH between 6.65 to 7.5 occurs on the addition of one mole of H^+ per mole of the complex. This corresponds to the formation of dibasic complex $[Mo(OH)_2(CN)_4]^{2-}$

$$K_3[MoO(OH)(CN)_4]^{3-} + H_2O = K_2[Mo(OH)_2(CN)_4]^{2-} + KOH$$
$$HCl + KOH = KCl + H_2O$$

$$K_3[MoO(OH)(CN)_4] + HCl = K_2[Mo(OH)_2(CN)_4] + KCl$$

The pH at the mid-point of the first segment is taken to be equal to pK_3'.

When 3 equivalents of H^+ are added, a second inflection point lying at a pH between 2.75 to 5.5 occurs and a basic cyanide is formed.

$$K_2[Mo(OH)_2(CN)_4] + 2HCl = Mo(OH)_2(CN)_2 + 2KCl + 2HCN$$
$$2KOH + 2HCl = 2KCl + 2H_2O$$

$$K_2[Mo(OH)_2(CN)_4] + 2HCl = Mo(OH)_2(CN)_2 + 2KCl + 2HCN$$

The second inflection point was not as sharp as the first one. The pH at the mid-point of the second segment is taken to be equal to pK_2'. Addition of more acid followed the appearance

of a green gel like precipitate, which on the addition of more acid, started dissolving. Thus at the end of titration (at about 10 equivalents of H^+) the solution was clear and its colour was brownish-green.

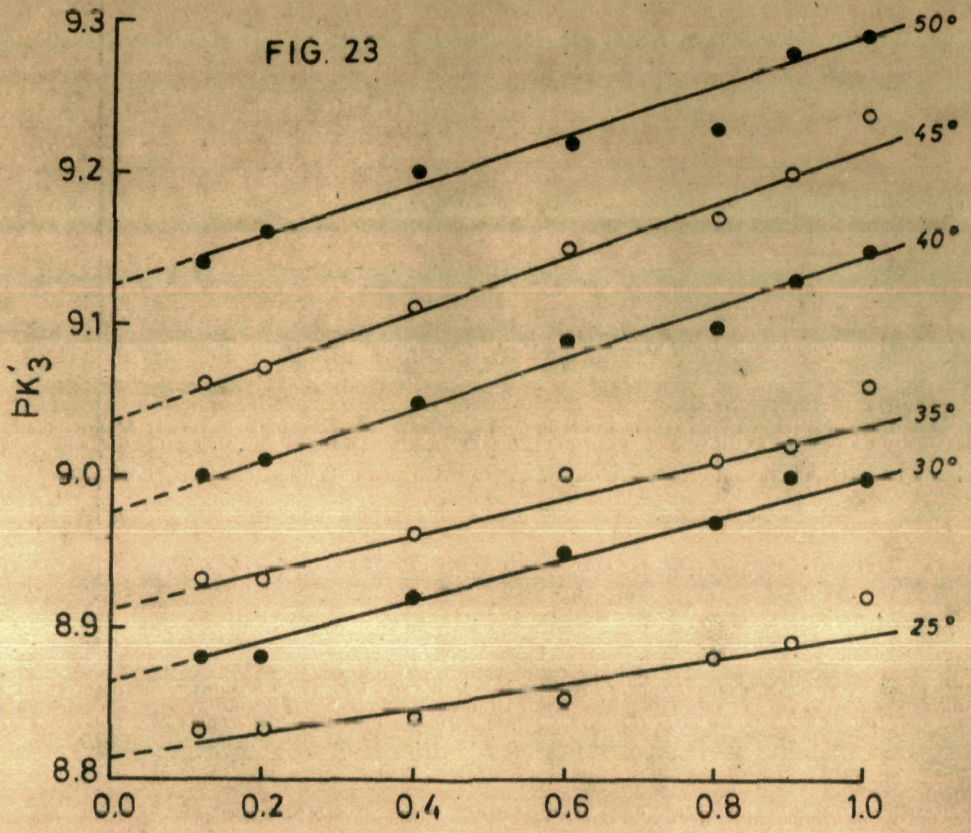
This latter sequence of changes may be explained on the basis of formation of a colloidal solution of the basic molybdenum cyanide. This coagulates giving a green precipitate separates out. This substance is a product of the break down of the dibasic complex in accordance with the reaction:

$$[Mo(OH)_2(CN)_4]^{2-} + 2\,H^+ \longrightarrow Mo(OH)_2(CN)_2 + 2HCN$$

This basic cyanide seems to dissolve slowly in excess of the acid:

$$Mo(OH)_2(CN)_2 + 2H^+ \longrightarrow MoO^{2+} + H_2O + 2HCN$$

Litvinchuk and Mikhalevich determined the acid dissociation constants (pK_3') at 16°C from hydrolysis studies to be 8.74[1]. This value has been determined by us for a wide range of temperature and ionic strength, in good agreement with the value reported from hydrolysis data (vide table 23). The pK_3' values at each temperatures has been extrapolated to zero ionic strength (μ) (fig.23) and the standard thermodynamic constants for the respective reaction has been obtained (table 24).



Extrapolation to zero ionic strength of PK'_3 values observed at different temperatures

TABLE -23.

pK_3' values obtained at different temperatures and ionic strengths.

Temperatures (°C)	Ionic strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
25	8.83	8.83	8.84	8.85	8.88	8.89	8.92
30	8.88	8.88	8.92	8.95	8.97	9.00	9.00
35	8.93	8.93	8.96	9.00	9.01	9.02	9.06
40	9.00	9.01	9.05	9.09	9.10	9.13	9.15
45	9.06	9.07	9.11	9.15	9.17	9.20	9.24
50	9.14	9.16	9.20	9.22	9.23	9.28	9.29

(Fig.23)

TABLE - 24.

pK_3' values obtained from extrapolation are:

Temp.(°C)	25	30	35	40	45	50
pK_3'	8.81	8.86	8.90	8.97	9.04	9.13

The variation of pK_3' with temperature follows the Harned-Robinson equation[4].

$$pK_3' = A^*/T - D^* + C^*T \quad \ldots\ldots\ldots \quad (1)$$

The pK_3' data were treated by a least-squares method in which the fit of the data to a wide range of sets of possible values could be tested and the significance of any particular value assessed. The programme was run on an IBM 1130 computer. The following equation was obtained.

$$pK_3' = (1730.72/T) - 6.1900 + 0.0308T \quad \ldots\ldots\ldots \quad (2)$$

The maximum deviations in pK_3' values obtained from this equation, and those found experimentally, lie within $\pm$ 0.02 unit. Thermodynamic quantities Δ^oG, ΔH^o, ΔS^o and ΔC_p^o for the ionisation process were calculated from the constants of equation(1), using the following thermodynamic formulae[5]

$$\Delta G^o = A' - D'T + C'T^2 \quad \ldots\ldots\ldots \quad (3)$$

$$\Delta H^o = A' - C'T^2 \quad \ldots\ldots\ldots \quad (4)$$

$$\Delta S^o = D' - 2C'T \quad \ldots\ldots\ldots \quad (5)$$

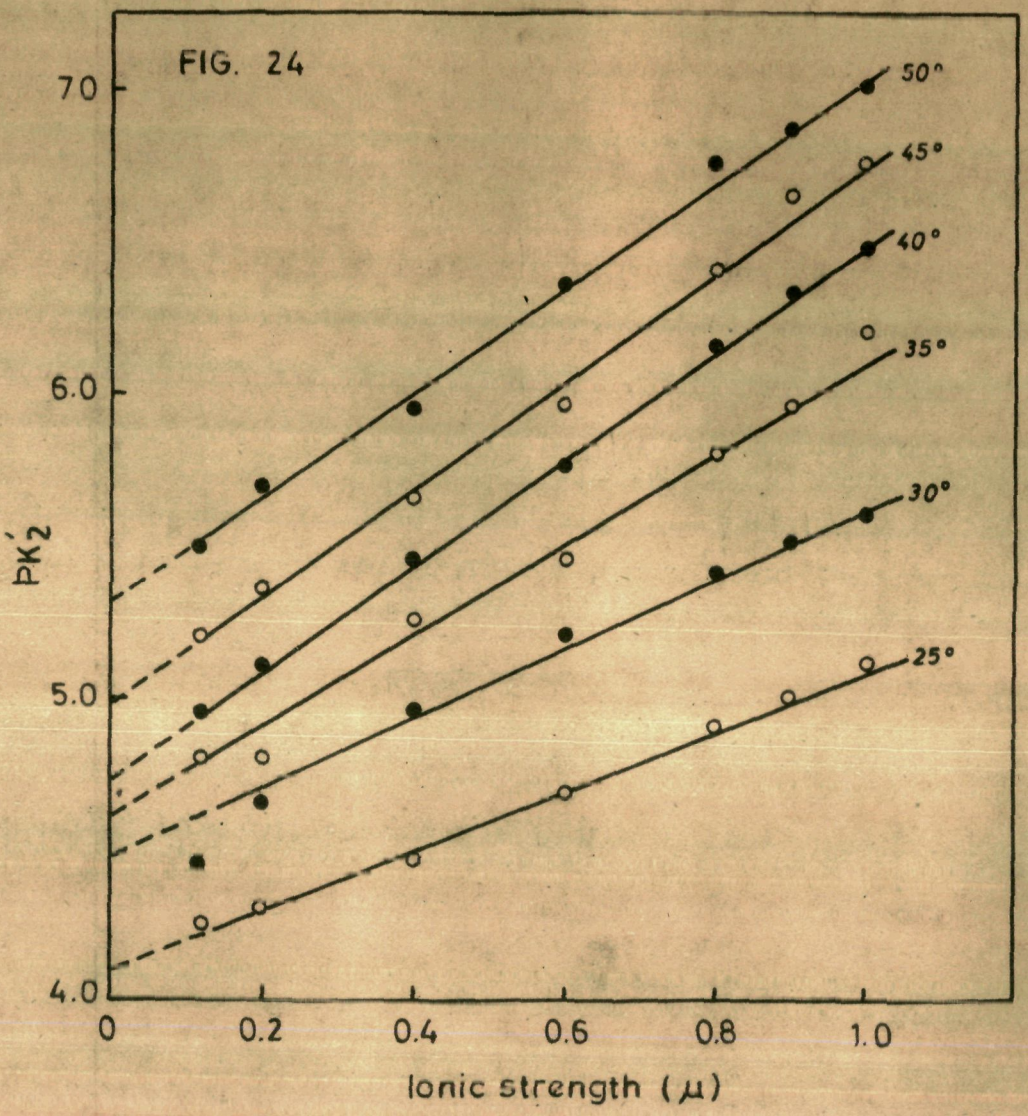
$$\Delta C_p^o = - 2C'T \quad \ldots\ldots\ldots \quad (6)$$

where $A' = 2.3026\ RA^*$, $C' = 2.3026\ RC^*$, $D' = 2.3026\ RD^*$.
The values of thermodyenamic parameters at 30°C are given in (table 25).

TABLE-25.

Thermodynamic quantities for the dissociation of oxohydroxo-cyanomolybdic acid at 30°C.

ΔG^o(Cal.mole^{-1})	ΔH^o(Cal.mole^{-1})	ΔS^o(Cal.deg.$^{-1}$mole^{-1})	ΔC_p^o(Cal.deg.$^{-1}$mole^{-1})
+ 12264	- 5016	-57.07	- 85.39



Extrapolation to zero ionic strength of pK'_2 values observed at different temperatures

The second acid dissociation constant (pK_2') has also been determined by us for a wide range of temperature and ionic strength (table 26).

The pK_2' values at each temperature has been extrapolated to zero ionic strength (μ) (Fig.24) and the standard thermodynamic constants for the respective reaction has been obtained (table 27).

T A B L E -26.

pK_2' values obtained at different temperature and ionic strength

Temperatures (°C)	Ionic strength						
	0.12	0.2	0.4	0.6	0.8	0.9	1.0
25	4.25	4.30	4.45	4.65	4.90	5.00	5.15
30	4.45	4.65	4.95	5.20	5.40	5.50	5.60
35	4.80	4.80	5.25	5.45	5.80	5.95	6.20
40	4.95	5.10	5.45	5.75	6.15	6.30	6.45
45	5.20	5.35	5.65	5.95	6.40	6.65	6.75
50	5.50	5.70	5.95	6.35	6.70	6.85	7.00

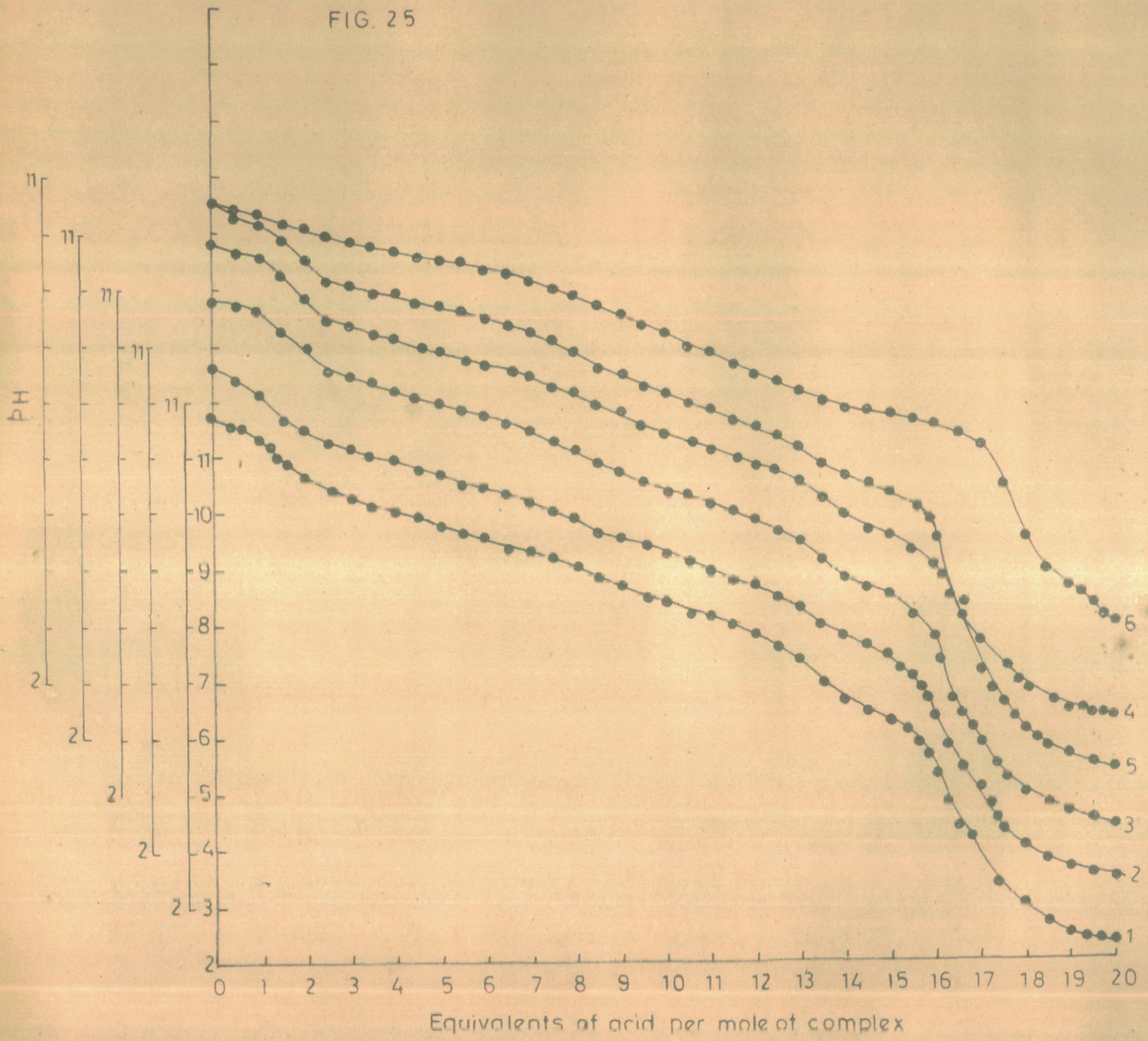
Fig.(24)

T A B L E -27.

pK_2' values obtained from extrapolation are:

Temp.(°C)	25	30	35	40	45	50
pK_2'	4.10	4.45	4.65	4.75	4.95	5.30

FIG. 25


pH
11
10
9
8
7
6
5
4
3
2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Equivalents of acid per mole of complex
1
2
3
4
5
6

(B) TETRAPOTASSIUM DIOXO-TETRACYANOTUNGSTATE (IV)

TABLE-28.

Vol.of TCT = 20.0 ml.
Concn.of TCT = 0.025M
Concn.of HCl = 0.1M
Temperature = 30°C

Vol.of HCl added (ml.)	pH					
	Ionic Strength					
	0.25	0.4	0.5	0.6	0.8	1.0
0.0	11.70	11.60	11.80	11.80	11.55	10.55
0.2	11.65	11.65	11.80	11.80	11.50	10.55
0.4	11.50	11.50	11.75	11.70	11.50	10.50
0.6	11.50	11.35	11.70	11.65	11.45	10.45
0.8	11.40	11.25	11.65	11.60	11.35	10.25
1.0	11.30	11.10	11.60	11.55	11.30	10.15
1.2	11.15	10.95	11.55	11.45	11.20	10.10
1.4	11.00	10.75	11.45	11.35	11.05	10.10
1.6	10.85	10.65	11.25	11.20	10.90	10.10
1.8	10.70	10.55	11.15	11.00	10.65	10.05
2.0	10.60	10.45	10.95	10.85	10.50	10.05
2.2	10.50	10.40	10.75	10.70	10.35	10.00
2.4	10.40	10.30	10.65	10.55	10.20	9.95
2.6	10.35	10.25	10.50	10.45	10.15	9.90
2.8	10.30	10.15	10.45	10.35	10.05	9.85
3.0	10.25	10.15	10.45	10.35	10.05	9.85
3.2	10.20	10.15	10.45	10.35	10.00	9.85

(Contd.)

TABLE -28.(Contd.)

3.4	10.15	10.05	10.35	10.25	9.95	9.80
3.6	10.10	10.00	10.35	10.20	9.90	9.75
3.8	10.05	9.95	10.25	10.15	9.85	9.70
4.0	10.00	9.90	10.15	10.10	9.90	9.65
4.2	10.00	9.85	10.10	10.05	9.85	9.65
4.4	9.95	9.80	10.05	10.00	9.85	9.65
4.6	9.90	9.75	10.00	9.95	9.70	9.55
4.8	9.85	9.70	9.95	9.90	-	9.55
5.0	9.75	9.65	9.90	9.85	9.65	9.50
5.2	9.70	9.65	9.85	9.80	9.60	9.45
5.4	9.65	9.55	9.85	9.75	9.55	9.40
5.6	9.60	9.50	9.80	9.70	9.50	9.40
5.8	9.55	9.45	9.75	9.65	9.45	9.35
6.0	9.50	9.40	9.70	9.65	9.45	9.30
6.2	9.45	9.35	9.70	9.65	9.40	9.25
6.4	9.40	9.35	9.65	9.60	9.35	9.20
6.6	9.35	9.30	9.55	9.50	9.30	9.20
6.8	9.35	9.25	9.55	9.45	9.25	9.15
7.0	9.30	9.15	9.45	9.40	9.20	9.10
7.2	9.25	9.10	9.40	9.35	9.15	9.05
7.4	9.20	9.05	9.30	9.25	9.10	9.00
7.6	9.15	9.00	9.25	9.20	9.05	8.95

(Contd.)

T A B L E - 28.(Contd.)

7.8	9.05	8.95	9.15	9.15	8.95	8.90
8.0	9.00	8.85	9.10	9.10	8.85	8.85
8.2	8.95	8.80	9.00	9.00	8.75	8.75
8.4	8.85	8.75	8.85	8.95	8.60	8.70
8.6	8.75	8.65	8.85	8.85	8.55	8.65
8.8	8.70	8.60	8.80	8.80	8.45	8.55
9.0	8.65	8.55	8.70	8.75	8.40	8.50
9.2	8.55	8.45	8.65	8.65	-	8.50
9.4	8.50	8.40	8.55	8.60	8.30	8.45
9.6	8.45	8.35	8.50	8.50	8.25	8.30
9.8	9.40	8.30	8.45	8.45	8.15	8.25
10.0	8.35	8.25	8.35	8.35	8.10	8.15
10.2	8.30	8.15	8.35	8.30	8.05	8.10
10.4	8.25	8.10	8.35	8.25	7.95	8.10
10.6	8.15	8.05	8.30	8.20	7.90	7.95
10.8	8.15	8.00	8.25	8.15	7.85	7.90
11.0	8.15	7.95	8.15	8.10	7.80	7.80
11.2	8.15	7.85	8.10	8.05	7.75	7.75
11.4	8.00	7.80	8.05	7.90	7.65	7.70
11.6	7.95	7.75	8.00	7.90	7.60	7.65
11.8	7.90	7.65	7.95	7.85	7.55	7.50
12.0	7.80	7.65	7.85	7.80	7.50	7.45
12.2	7.75	7.60	7.80	7.75	7.45	7.40

(Contd.)

T A B L E - 28.(Contd.)

12.4	7.65	7.55	7.75	7.75	7.35	7.35
12.6	7.55	7.45	7.65	7.70	7.30	7.30
12.8	7.45	7.35	7.55	7.60	7.20	7.25
13.0	7.35	7.25	7.45	7.50	7.10	7.20
13.2	7.25	7.15	7.35	7.40	7.00	7.15
13.4	7.05	7.05	7.25	7.30	6.95	7.15
13.6	6.90	6.95	7.10	7.20	6.80	6.95
13.8	6.70	6.85	6.95	7.05	6.70	6.90
14.0	6.60	6.75	6.80	6.90	6.60	6.85
14.2	6.55	6.70	6.75	6.80	6.55	6.85
14.4	6.45	6.65	6.65	6.75	6.50	6.80
14.6	6.40	6.60	6.60	6.65	6.45	6.80
14.8	6.35	6.55	6.55	6.60	6.35	6.75
15.0	6.25	6.45	6.50	6.55	6.30	6.75
15.2	6.15	6.40	6.40	6.55	6.25	6.70
15.4	6.05	6.35	6.30	6.40	6.15	6.65
15.6	5.85	6.25	6.15	6.30	6.05	6.60
15.8	5.65	6.10	6.10	6.20	5.80	6.55
16.0	5.25	5.95	5.75	6.05	5.45	6.55
16.2	4.75	5.70	5.30	5.85	4.80	6.45
16.4	4.65	5.25	4.60	5.45	4.35	6.40

(Contd.)

T A B L E -28.(Contd.)

16.6	4.35	4.70	4.35	4.75	4.05	6.35
16.8	4.25	4.25	4.10	4.20	3.85	6.25
17.0	4.25	4.05	3.85	4.05	3.60	6.15
17.2	4.10	3.75	3.65	3.80	3.35	6.10
17.4	3.55	3.50	3.40	3.55	3.15	5.80
17.6	3.25	3.30	3.20	3.30	3.00	5.45
17.8	3.10	3.15	3.05	3.15	2.90	4.75
18.0	3.00	3.00	2.95	3.05	2.80	4.50
18.2	2.85	2.95	2.85	2.95	2.70	4.25
18.4	2.75	2.85	2.75	2.85	2.60	4.00
18.6	2.65	2.75	2.70	2.75	2.55	3.90
18.8	2.55	2.65	2.65	2.65	2.50	3.75
19.0	2.45	2.60	2.60	2.60	2.45	3.65
19.2	2.40	2.55	2.55	2.55	2.40	3.50
19.4	2.35	2.50	2.50	2.50	2.35	3.30
19.6	2.30	2.45	2.45	2.45	2.30	3.15
19.8	2.25	2.40	2.40	2.40	2.25	3.05
20.0	2.25	-	2.35	2.35	2.25	2.95

Fig.(25)Curve(I)Curve(II)Curve(III)Curve(IV)Curve(V) Curve(VI)

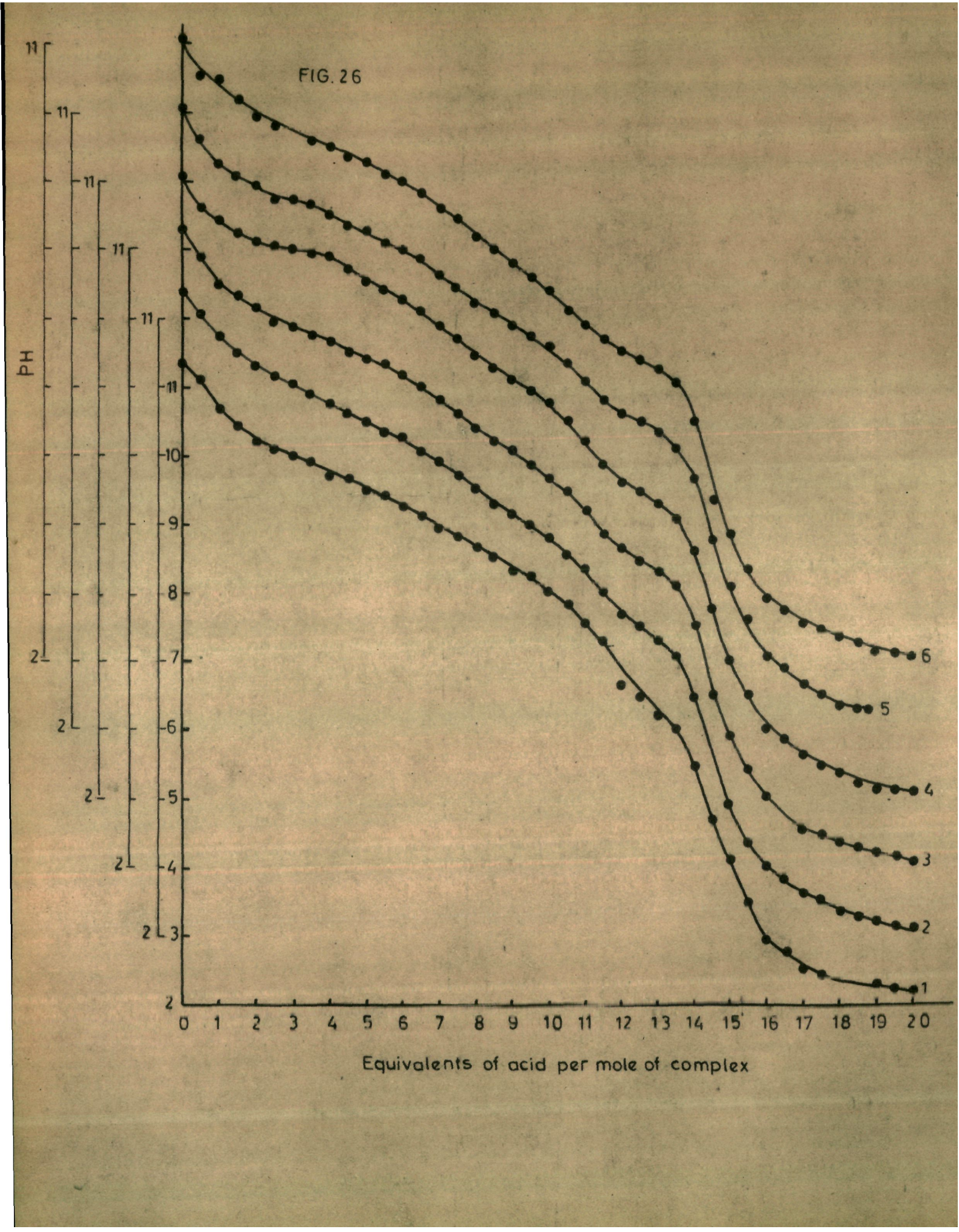


FIG. 26
pH
11
2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Equivalents of acid per mole of complex
1
2
3
4
5
6

T A B L E -29.

Vol.of TCT = 20.0 ml.
Concn.of TCT = 0.025M
Concn.of HCl = 0.1M
Temperature = 35°C

Vol.of HCl added (ml.)	pH					
	Ionic strength					
	0.25	0.4	0.5	0.6	0.8	1.0
0.0	11.35	11.40	11.30	11.05	11.05	11.05
0.5	11.10	11.05	10.90	10.65	10.60	10.55
1.0	10.65	10.75	10.50	10.45	10.25	10.50
1.5	10.45	10.50	10.35	10.25	10.05	10.20
2.0	10.20	10.30	10.15	10.10	9.95	9.95
2.5	10.10	10.15	9.95	10.05	9.75	9.80
3.0	10.00	10.05	9.90	10.00	9.75	9.80
3.5	9.90	9.90	9.75	9.95	9.65	9.60
4.0	9.75	9.75	9.65	9.90	9.50	9.50
4.5	9.65	9.60	9.50	9.70	9.35	9.35
5.0	9.50	9.50	9.40	9.55	9.25	9.25
5.5	9.40	9.35	9.35	9.40	9.10	9.10
6.0	9.25	9.25	9.15	9.30	9.00	9.00
6.5	9.10	9.05	9.00	9.10	8.85	8.80
7.0	8.90	8.90	8.80	8.90	8.65	8.60

(Contd.)

TABLE -29:(Contd.)

7.5	8.80	8.70	8.60	8.70	8.45	8.45
8.0	8.65	8.50	8.40	8.45	8.25	8.20
8.5	8.55	8.30	8.20	8.25	8.05	8.00
9.0	8.30	8.15	8.05	8.10	7.90	7.80
9.5	8.20	8.00	7.85	7.95	7.75	7.60
10.0	8.00	7.80	7.65	7.75	7.60	7.40
10.5	7.80	7.55	7.45	7.50	7.35	7.15
11.0	7.55	7.35	7.20	7.20	7.10	6.90
11.5	7.25	7.00	6.85	6.85	6.80	6.70
12.0	6.60	6.65	6.65	6.60	6.60	6.55
12.5	6.45	6.50	6.45	6.45	6.50	6.40
13.0	6.20	6.30	6.30	6.30	6.35	6.25
13.5	6.00	6.05	6.10	6.05	6.10	6.05
14.0	5.45	5.45	5.55	5.60	5.65	5.50
14.5	4.65	-	4.50	4.75	4.75	4.35
15.0	4.10	3.90	3.90	4.00	4.05	3.85
15.5	3.45	3.35	3.40	3.50	3.60	3.35
16.0	2.95	3.00	3.00	3.00	3.05	2.95
16.5	2.75	2.80	-	2.85	2.90	2.75
17.0	2.50	2.60	2.55	2.60	2.65	2.55
17.5	2.40	2.55	2.45	2.45	2.50	2.45
18.0	-	2.35	2.35	2.35	2.35	2.35
18.5	-	2.25	2.25	2.25	2.30	2.25
19.0	2.30	2.20	2.20	2.20	2.30	2.15
19.5	2.20	2.15	2.15	2.10	-	2.10
20.0	2.15	2.10	2.05	2.10	-	2.05
(Fig.26)	Curve(I)	Curve(II)	Curve(III)	Curve(IV)	Curve(V)	(Curve(VI)

FIG. 27

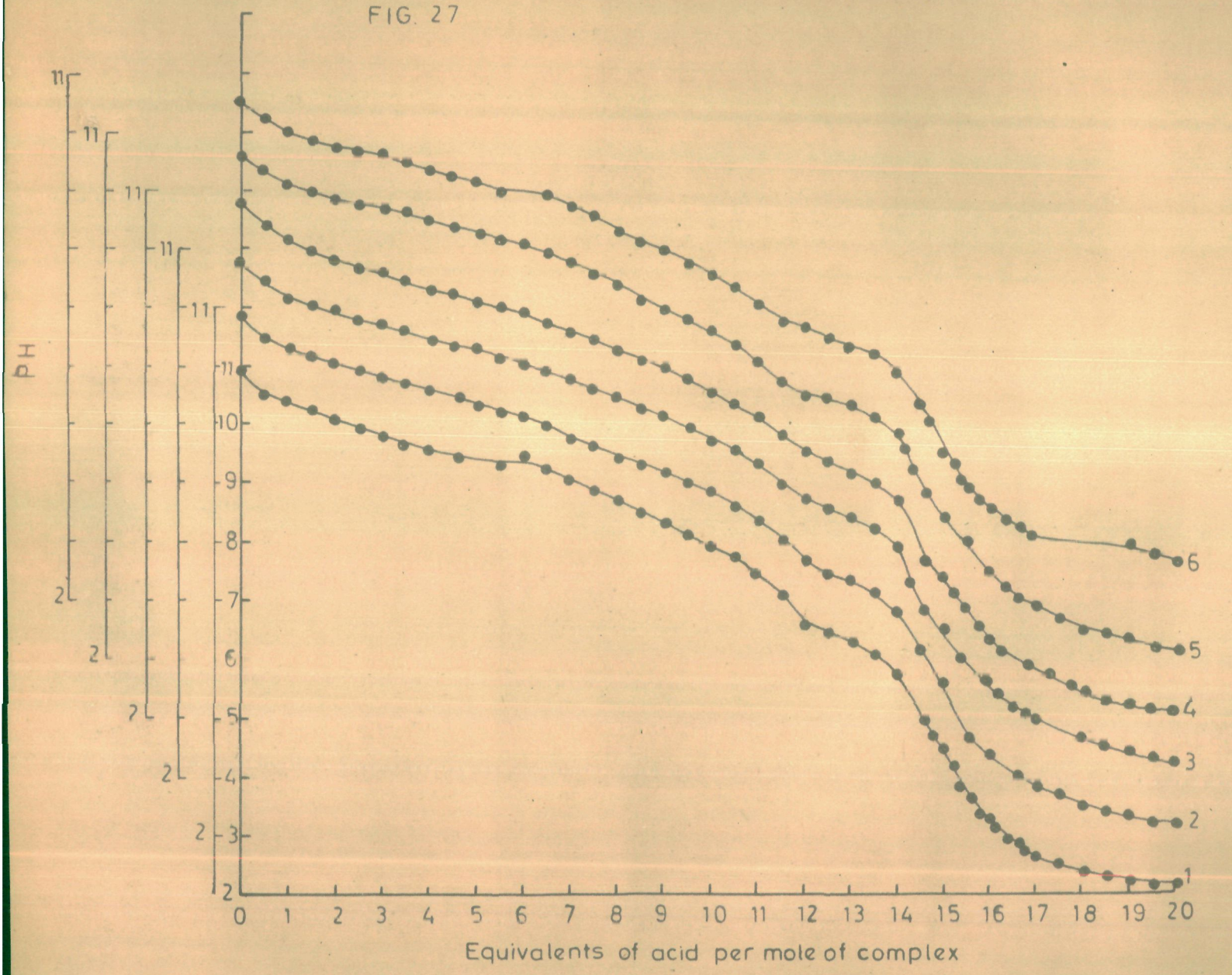

pH
11
10
9
8
7
6
5
4
3
2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Equivalents of acid per mole of complex
1
2
3
4
5
6

TABLE - 30.

Vol. of TCT = 20.0 ml.
Concn. of TCT = 0.025M
Concn. of HCl = 0.1M
Temperature = 40°C

Vol. of Hcl added (ml.)	pH — Ionic Strength					
	0.25	0.4	0.5	0.6	0.8	1.0
0.0	10.90	10.90	10.80	10.80	10.60	10.55
0.5	10.50	10.50	10.45	10.40	10.35	10.25
1.0	10.40	10.30	10.15	10.15	10.10	10.00
1.5	10.25	10.15	10.05	9.95	9.95	9.85
2.0	10.05	10.00	9.95	9.80	9.85	9.75
2.5	9.90	9.90	9.75	9.65	9.70	9.65
3.0	9.80	9.80	9.70	9.60	9.70	9.60
3.5	9.65	9.70	9.60	9.45	9.60	9.45
4.0	9.55	9.55	9.45	9.30	9.50	9.35
4.5	9.45	9.45	9.35	9.20	9.35	9.25
5.0	-	9.30	9.30	9.05	9.25	9.15
5.5	9.60	9.20	9.10	9.00	9.15	8.95
6.0	9.45	9.10	9.05	8.90	9.05	-
6.5	9.25	8.95	8.90	8.75	8.90	8.90

(Contd.)

TABLE - 30.(Contd.)

7.0	9.05	8.75	8.75	8.55	8.75	8.75
8.5	8.45	8.25	8.25	8.05	8.10	8.10
9.0	8.30	8.15	8.10	7.95	7.95	7.95
9.5	8.10	8.00	7.90	7.75	7.80	7.75
10.0	7.90	7.80	7.70	7.55	7.60	7.55
10.5	7.70	7.60	7.55	7.35	7.35	7.35
11.0	7.45	7.35	7.30	7.10	7.05	7.05
11.5	7.05	7.00	6.95	6.80	6.70	6.80
12.0	6.55	6.65	6.70	6.50	6.60	6.65
12.5	6.40	6.45	6.55	6.35	6.45	6.50
13.0	6.25	6.30	6.40	6.20	6.30	6.35
13.5	6.05	6.10	6.20	6.00	6.10	6.20
14.0	5.70	5.75	5.90	5.70	5.80	5.90
14.2	5.55	-	5.65	5.50	5.60	-
14.4	5.25	-	5.30	5.20	5.25	-
14.5	-	5.10	-	-	-	5.30
14.6	4.85	-	4.80	4.65	4.80	5.05
14.8	4.55	-	4.45	4.20	4.45	4.50
15.0	4.45	4.55	4.55	4.40	4.40	4.55
15.2	4.15	4.20	4.25	4.05	4.30	4.30
15.4	3.80	3.95	4.00	3.85	-	4.05
15.6	3.60	3.65	3.90	3.65	3.95	3.90

(Contd.)

T A B L E - 30(Contd.)

15.8	3.40	3.45	3.70	3.45	3.70	3.70
16.0	3.30	3.35	3.55	3.30	3.50	3.55
16.2	3.10	3.25	3.40	3.15	3.35	3.50
16.4	3.00	3.10	3.30	3.00	3.20	3.35
16.6	2.85	3.00	3.15	2.90	3.30	3.25
16.8	2.75	2.85	3.05	2.80	2.95	3.10
17.0	2.70	2.85	2.95	2.70	2.85	-
17.5	2.50	2.65	-	2.55	2.65	-
18.0	2.40	2.50	2.60	2.45	2.50	-
18.5	2.30	2.40	2.50	2.25	2.40	-
19.0	2.25	2.30	2.40	2.20	2.30	3.00
19.5	2.15	2.20	2.30	2.10	2.20	2.75
20.0	2.10	2.15	2.20	2.05	2.15	2.60
Fig.(27)	Curve(I)	Curve(II)	Curve(III)	Curve(IV)	Curve(V)	Curve(VI)

FIG. 28

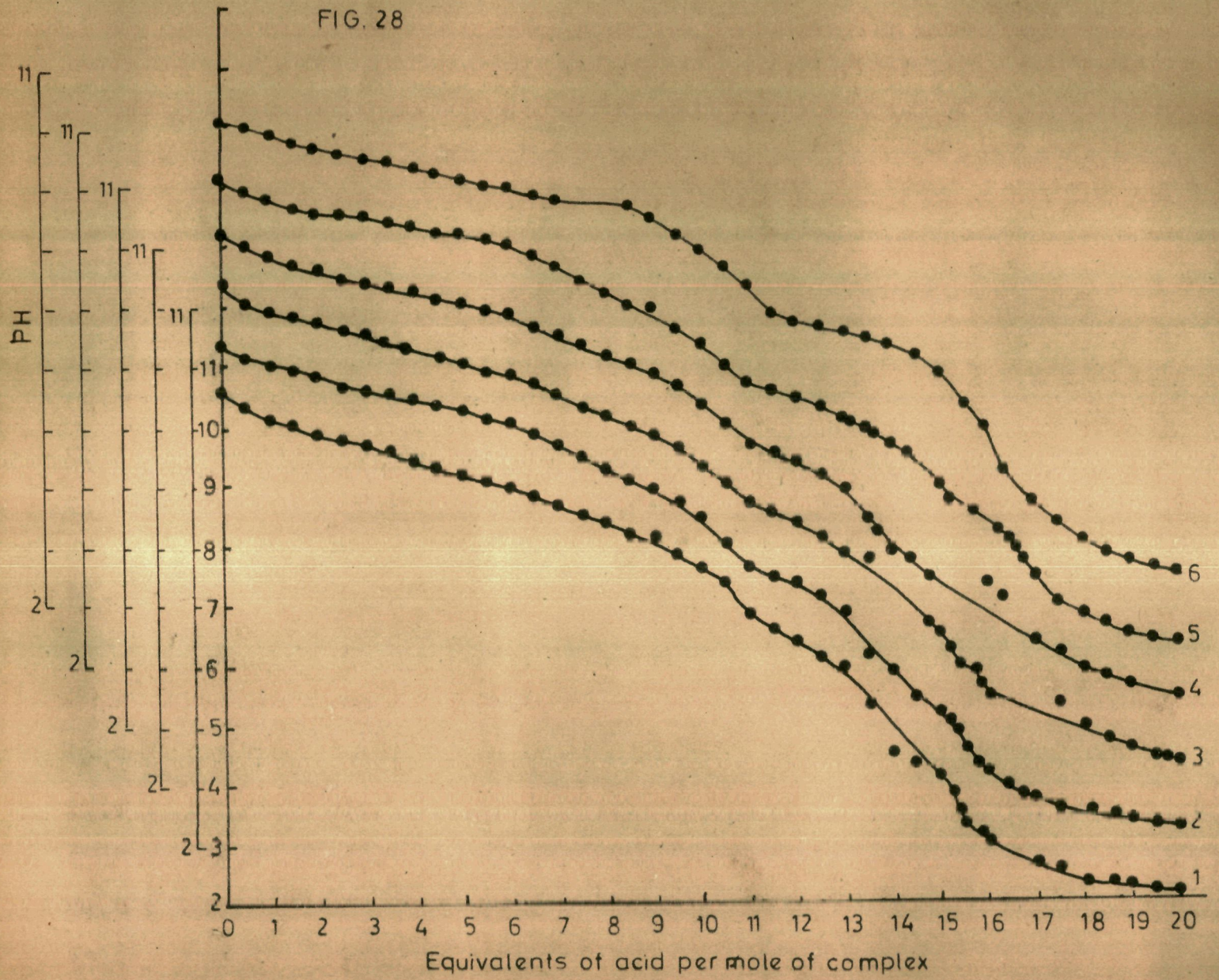

pH
11
2
-0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Equivalents of acid per mole of complex
1
2
3
4
5
6

TABLE-31

Vol. of TCT = 20.0 ml.
Concn. of TCT = 0.025M
Concn. of HCl = 0.1M
Temperature = 45°C

Vol. of HCl added (ml.)	pH					
	Ionic Strength					
	0.25	0.4	0.5	0.6	0.8	1.0
0.0	10.60	10.40	10.40	10.25	10.15	10.10
0.5	10.30	10.15	10.05	10.05	9.95	10.00
1.0	10.10	10.05	9.90	9.85	9.80	9.90
1.5	10.00	9.95	9.85	9.70	9.65	9.75
2.0	9.85	9.80	9.70	9.60	9.60	9.65
2.5	9.75	9.65	9.60	9.45	9.55	9.55
3.0	9.70	9.60	9.55	9.45	9.50	9.50
3.5	9.55	9.55	9.40	9.30	9.40	9.40
4.0	9.40	9.45	9.30	9.25	9.35	9.30
4.5	9.30	9.35	9.15	9.10	9.25	9.20
5.0	9.15	9.25	9.05	9.05	9.20	9.10
5.5	9.05	9.10	8.90	8.95	9.10	9.00

(Contd.)

T A B L E -31.(Contd.)

6.0	8.95	9.00	8.85	8.85	9.00	9.00
6.5	8.80	8.85	8.70	8.65	8.85	8.85
7.0	8.65	8.65	8.50	8.50	8.65	8.75
7.5	8.50	8.45	8.30	8.35	8.40	9.20
8.0	8.35	8.25	8.15	8.15	8.20	9.00
8.5	8.15	8.05	8.00	8.00	8.00	8.70
9.0	8.15	7.90	7.80	7.85	8.00	8.45
9.5	7.80	7.70	7.60	7.65	7.60	8.15
10.0	7.60	7.40	7.30	7.35	7.35	7.90
10.5	7.30	7.00	7.00	7.00	7.00	7.65
11.0	6.80	6.60	6.65	6.65	6.65	7.30
11.5	6.50	6.45	6.50	6.50	6.55	6.85
12.0	6.35	6.30	6.35	6.35	6.45	6.70
12.5	6.15	6.10	6.10	6.15	6.30	6.60
13.0	5.90	5.80	5.85	5.90	6.10	6.55
13.2	-	-	-	-	6.00	-
13.5	5.30	5.10	5.25	5.40	5.90	6.45
13.6	-	-	-	-	5.80	-
13.8	-	-	-	-	5.65	-
14.0	4.50	4.85	4.80	4.85	5.75	6.30

(Contd.)

TABLE - 31.(Contd.)

14.2	-	-	4.70	4.65	5.70	-
14.4	4.30	-	4.80	4.75	5.50	-
14.5	-	4.40	-	-	5.10	6.15
14.8	4.25	-	4.65	4.45	-	-
15.0	4.05	5.15	4.50	-	5.00	5.85
15.2	3.80	4.00	4.25	-	4.70	-
15.4	3.50	3.85	3.95	4.60	4.80	-
15.6	3.25	3.55	3.90	-	4.70	5.25
15.8	3.10	3.30	3.90	-	4.55	-
16.0	2.95	3.15	4.10	4.35	4.20	4.90
16.2	2.85	3.05	3.95	-	4.00	-
16.4	2.80	2.95	4.00	4.10	3.85	4.15
16.6	2.70	2.85	4.00	-	3.65	-
16.8	2.65	2.75	4.00	-	3.65	-
17.0	2.60	2.70	4.00	3.35	3.40	3.70
17.5	2.50	2.55	3.30	3.15	2.95	3.35
18.0	2.30	2.60	2.95	2.90	2.75	3.05
18.5	2.30	2.45	2.70	2.75	2.60	2.80
19.0	2.25	2.35	2.55	2.60	2.45	2.70
19.5	2.15	2.25	2.40	-	2.35	2.55
20.0	2.10	2.20	2.30	2.45	2.30	2.45
Fig.(28)	Curve(I)	Curve(II)	Curve(III)	Curve(IV)	Curve(V)	Curve(VI)

FIG. 29

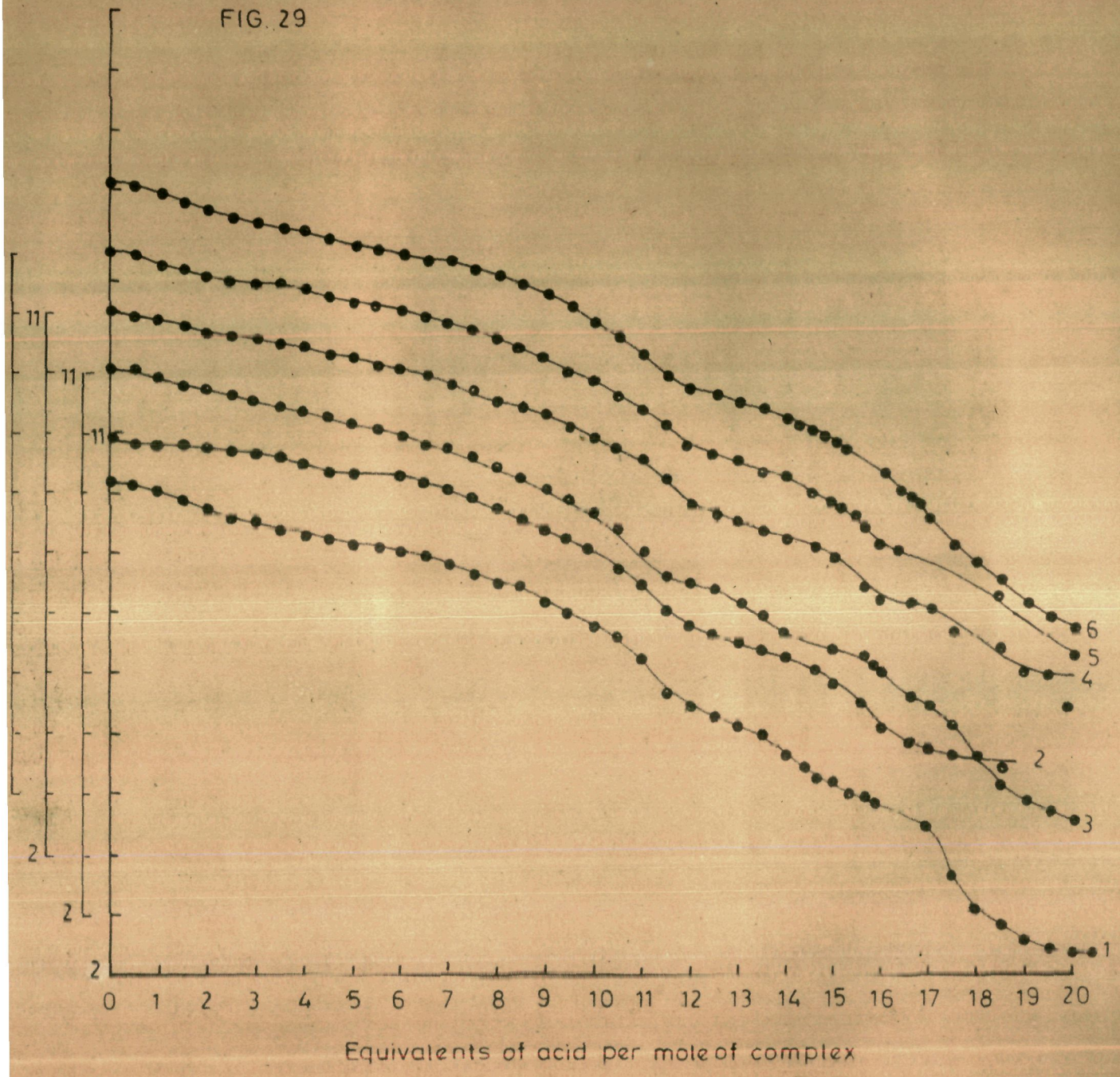

11
11
11
2
2
2
6
5
4
2
3
1
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Equivalents of acid per mole of complex

TABLE - 32.

Vol. of TCT = 20.0 ml.
Concn. of TCT = 0.025M
Concn. of HCl = 0.1M
Temperature = 50°C.

Vol. of HCl added (ml.)	pH					
	Ionic Strength					
	0.25	0.4	0.5	0.6	0.8	1.0
0.0	10.20	9.85	10.05	10.00	9.95	10.15
0.5	10.10	9.75	10.00	9.95	9.90	10.10
1.0	10.00	9.75	9.90	9.85	9.75	9.95
1.5	9.85	9.80	9.75	9.75	9.65	9.80
2.0	9.70	9.70	9.65	9.65	9.55	9.65
2.5	9.55	9.65	9.55	9.55	9.45	9.55
3.0	9.50	9.65	9.50	9.55	9.45	9.50
3.5	9.35	9.55	9.40	9.45	9.45	9.40
4.0	9.25	9.45	9.30	9.35	9.35	9.30
4.5	9.20	9.30	9.20	9.25	9.25	9.20
5.0	9.10	9.30	9.10	9.15	9.15	9.10
5.5	9.05	9.10	9.00	9.05	9.05	9.00
6.0	9.00	9.25	9.95	9.00	9.00	8.95
6.5	8.90	9.15	8.85	8.90	8.90	8.85
7.0	8.75	9.00	8.70	8.75	8.75	8.85

(Contd.)

T A B L E -32.(Contd.)

7.5	8.60	8.85	8.55	8.65	8.65	8.70
8.0	8.45	8.70	8.40	8.50	8.50	8.60
8.5	8.40	8.50	8.20	8.35	8.35	8.40
9.0	8.15	8.35	8.05	8.25	8.20	8.25
9.5	8.00	8.15	7.85	8.05	8.00	8.05
10.0	7.75	7.95	7.60	7.90	7.80	7.80
10.5	7.55	7.70	7.30	7.70	7.60	7.55
11.0	7.20	7.40	7.00	7.50	7.40	7.25
11.5	6.65	7.05	6.60	7.20	7.10	6.90
12.0	6.40	6.75	6.45	6.80	6.75	6.70
12.5	6.25	6.60	6.35	6.60	6.60	6.60
13.0	6.10	6.50	6.15	6.50	6.50	6.50
13.5	5.90	6.35	5.95	6.35	6.35	6.40
13.8	-	-	5.80	-	-	-
14.0	5.60	6.25	5.65	6.20	6.25	6.25
14.2	5.50	-	5.50	6.15	6.15	6.20
14.4	5.45	-	5.25	6.10	6.10	6.10
14.6	5.25	6.05	5.10	6.05	6.00	6.05
1.48	5.00	-	5.15	6.00	5.95	5.95
15.0	5.15	5.85	5.35	5.90	5.85	5.85
15.2	4.90	-	5.05	5.70	5.75	5.70
15.4	5.00	-	-	-	5.60	5.45

(Contd.)

T A B L E - 32(Contd.)

15.6	4.95	5.50	5.30	5.40	5.40	5.20
15.8	4.75	-	5.15	-	5.05	5.00
16.0	5.60	5.05	5.00	5.20	5.10	4.75
16.2	5.45	-	4.65	-	-	5.20
16.4	5.10		4.65	-	-	5.00
16.6	4.85	4.85	4.65	5.20	5.00	4.95
16.8	4.75	-	4.65	-	-	4.75
17.0	4.45	4.70	4.50	5.05	5.15	4.55
17.5	3.65	4.65	4.15	4.65	5.10	4.45
18.0	3.10	4.60	3.60	-	4.85	4.00
18.5	2.75	4.35	3.10	4.35	4.25	3.55
19.0	2.55	3.50	2.85	4.00	4.15	3.15
19.5	2.40	3.10	2.65	3.95	3.90	2.95
20.0	2.30	2.85	2.50	3.40	3.30	2.75

Fig.(29) Curve(I) Curve(II) Curve(III) Curve(IV) Curve(V) Curve(VI)

D I S C U S S I O N

The potentiometric titrations of TCT(IV) with hydrochloric acid show no sharp inflection point. On addition of one mole of H^+ to the complex ion, in general pH changes from 11.5 to 9.85. Further this change is quite gradual. The reaction corresponds to the $K_3[WO(OH)(CN)_4]$ is presumed to be formed.

$$K_4[WO_2(CN)_4] + HOH = K_3[WO(OH)(CN)_4] + KOH$$
$$KOH + HCl = KCl + H_2O$$

$$K_4[WO_2(CN)_4] + HCl = K_3[WO(OH)(CN)_4] + KCl$$

The hydrolysibility difference between $[WO_2(CN)_4]^{-4}$ and $[WO(OH)(CN)_4]^{-3}$ is such that it does not allow a sharp change in pH.

Further addition of one mole of H^+ corresponds to the formation of dibasic complex $[W(OH)_2(CN)_4]^{2-}$. Again, no sharp change in pH occurs in this case as well. The reaction seems to be

$$K_3\ WO(OH)(CN)_4 + HOH = K_2[W(OH)_2(CN)_4] + KOH$$
$$KOH + HCl = KCl + H_2O$$

$$K_3[WO(OH)(CN)_4] + HCl = K_2[W(OH)_2(CN)_4] + KCl$$

Further addition of one equivalent of H^+ again results into

a small change in pH, probably due to the formation of $[W(OH)_2(CN)_3]^{-1}$

$$[W(OH)_2(CN)_4]^{2-} + H^+ \longrightarrow [W(OH)_2(CN)_3]^{-1} + HCN$$

At about 3.35 equivalents of H^+, a fairly sharp change in pH occurs. During this titration it was observed that precipitation started when addition was continued after 3.0 equivalents. The precipitate was quite thick and gelatinous and dark green in colour. This seems to correspond to the formation of $W(OH)_2(CN)_2$. The inflection occurs at 3.35 equivalents instead of 4 equivalents of H^+ due to the incomplete conversion of $[W(OH)_2(CN)_3]^{-1}$ into the inner complex $W(OH)_2(CN)_2$. On addition of an excess of acid (about 20 equivalents of H^+) the gelatinous precipitate dissolves to give a clear solution. This sequence of change is quite analogous to the one observed in the case of tetracyanomolybdate(IV). As the inflection occurs at 3.5 equivalents of acid instead of 4 equivalents, from this titration curves one can not get the exact value of the dissociation constant.

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3. C.W.G. Kaye, H.T. Laby, "Physical and Chemical constants," Longmans,London 12th edition, (1959) 148.
4. H.S. Harned and A.R. Robinson, Trans. Faraday Soc., 36 (1940) 973.
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C H A P T E R - III:

Composition of Ag, Cu and Ni ammine complexes of Tripotassium oxo-hydroxotetracyanomolybdate (IV).

The existing literature shows that little work has been done on the interaction of ammine complexes with complex cyanides. Mikhalevich and Litvinchuk[1] made noticeable contribution in this direction. He studied the interaction of silver and of copper ammines with tetrapotassium dioxotetracyanotungstate(IV)(TCT).

The aim of the present investigation is to study the composition of silver, copper, nickel and cobalt ammines of tripotassium oxohydroxotetracyanomolybdate(IV)(TCM), nickel and cobalt ammines of tetrapotassium dioxotetracyanotungstate(IV)(TCT), employing physico-chemical methods. The physical methods have certain advantages over the method of chemical analysis in as far as they not only provide precize information about the composition of the freshly precipitated complex but are able to eliminate the errors. The physico-chemical methods used in these investigations were potentiometry and conductometry.

The conductometric titration method is well suited for the study of acid-base, displacement and precipitation reactions. A slow separation of precipitate; with consequent supersaturation of the solution and removal of the titrated solute by adsorption on the precipitate limits the usefulness

of this method. The conductometric titrations may sometimes be used in connection with coloured solution, such as dyestuffs, in which ordinary indicators can not be used. It can also be used in certain cases where potentiometric method fails.

EXPERIMENTAL

The potassium salts of TCM and TCT(IV) were prepared and standardised as described earlier(Chapter I). Stock solutions of 0.1M copper and nickel ammines were prepared by dissolving AnalaR (B.D.H.) grade cupric chloride and nickel chloride in 1M ammonia. Fresh solution of silver ammine (0.01M) was prepared by dissolving AnalaR (B.D.H.) grade sample of silver nitrate in 1M ammonia. Solution of cobalt ammine was also prepared by dissolving A.R.(B.D.H.) grade cobaltous nitrate in highly concentrated ammonia. Solution of silver ammine were always kept in dark.

Apparatus:- Pye Precision Vernier Potentiometer (Cat.No.7568) in conjunction with a ballistic galvanometer was employed for potential measurements. A bright platinum/calomel electrode was used as indicator electrode and saturated electrode as the reference electrode.

All the measurements were made in a dark room. To obviate air oxidation, each set of the experiment was performed under a nitrogen atmosphere.

Both, direct (the metal ammine in the cell) and reverse (TCM and TCT solution in the cell) titrations were performed at varying concentrations. The direct as well as the reverse titrations of cobalt and nickel ammines with TCT and the direct and reverse titrations of cobalt ammines with TCM were not successful.

The observations of direct and reverse potentiometric titrations are recorded in the following tables.

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FIG. 30

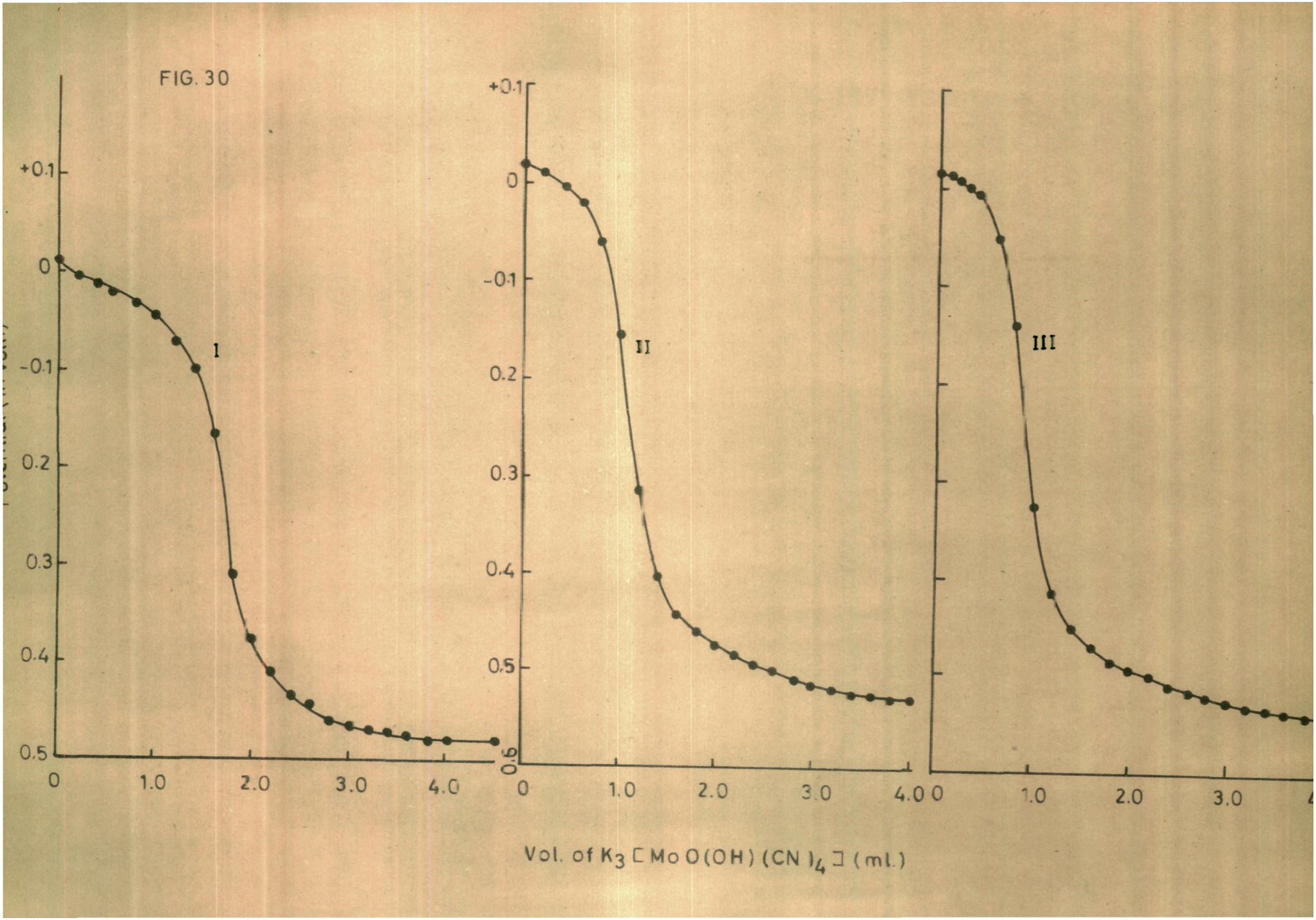


TABLE - 33.

Vol. of $[Ag(NH_3)_2]^+$ = 20.0 ml.
Strength of TCM = 2.5×10^{-2}M.

Vol.of TCM added(ml.)	Potential (vs.S.C.E., volt) $[Ag(NH_3)_2]^+ = 1.0\times10^{-2}$M	$= 6.67\times10^{-3}$M	$= 5.0\times10^{-3}$M
0.0	+0.01300	+0.02000	+0.01545
0.1	-	-	0.01443
0.2	-0.01100	0.01000	0.00884
0.3	-	-	0.00333
0.4	0.01456	-0.00553	-0.00608
0.6	0.02131	0.02416	0.05228
0.8	0.03106	0.06264	0.14341
1.0	0.04678	0.15145	0.32927
1.2	0.07255	0.31454	0.41514
1.4	0.10362	0.40454	0.45256
1.6	0.16728	0.44349	0.47346
1.8	0.31000	0.46268	0.48646
2.0	0.37930	0.47761	0.49517
2.2	0.41606	0.48662	0.50317
2.4	0.43506	0.49662	0.51100
2.6	0.44900	0.50405	0.51584
2.8	0.46000	0.51019	0.52184

(Contd.)

T A B L E - 33 (Contd.)

3.0	0.46528	0.51519	0.52644
3.2	0.47053	0.52019	0.53061
3.4	0.47458	0.52419	0.53389
3.6	0.47674	0.52839	0.53746
3.8	0.47847	0.53049	0.54087
4.0	0.48100	0.53400	0.54387
4.5	0.48772	-	-
Fig.(30)	Curve(I)	Curve(II)	Curve(III)

Curve (I): 20 ml.of 1.0×10^{-2}M $\left[Ag(NH_3)_2\right]^+$ = 2.0ml.of 2.5×10^{-2}M TCM

Curve (II): 20 ml.of 6.67×10^{-3}M $\left[Ag(NH_3)_2\right]^+$ = 1.4ml.of 2.5×10^{-2}M "

Curve (III): 10 ml.of 5.0×10^{-3}M $\left[Ag(NH_3)_2\right]^+$ = 1.0ml.of 2.5×10^{-2}M "

FIG. 31

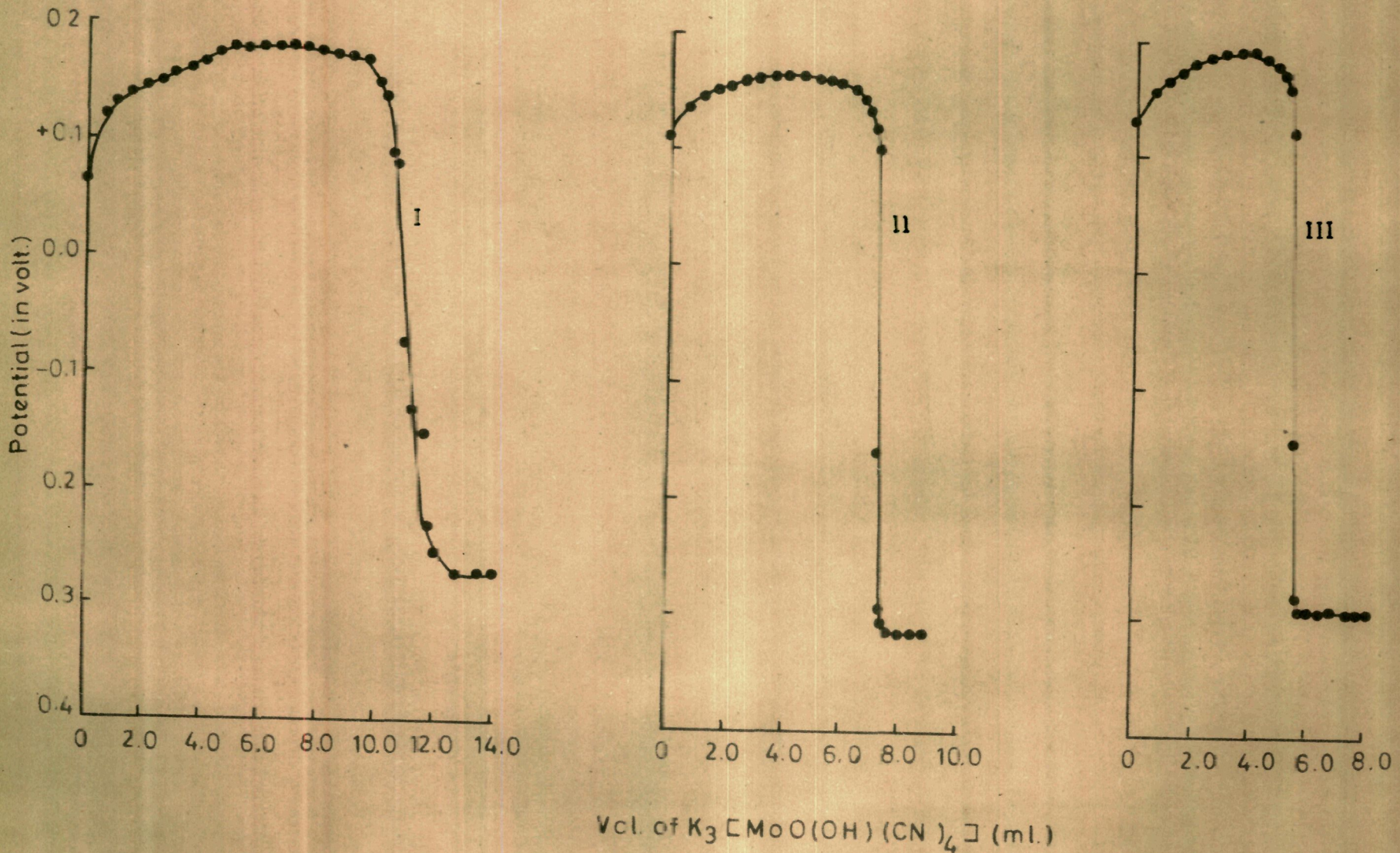

0.2
+0.1
0.0
-0.1
0.2
0.3
0.4
Potential (in volt.)
I
II
III
0 2.0 4.0 6.0 8.0 10.0 12.0 14.0
0 2.0 4.0 6.0 8.0 10.0
0 2.0 4.0 6.0 8.0
Vol. of $K_3[MoO(OH)(CN)_4]$ (ml.)

TABLE - 34

Vol.of $[Cu(NH_3)_4]^{2+}$ = 20.0 ml.

Strength of TCM = 2.5×10^{-2}M

Vol.of TCM added(ml.)	Potential (vs. S.C.E. volt)		
	$[Cu(NH_3)_4]^{2+} = 2.5\times10^{-2}$M	$= 1.667\times10^{-2}$M	$= 1.25\times10^{-2}$M
0.0	+0.06749	+0.11352	+0.13127
0.5	0.12412	0.13817	0.15627
1.0	0.13400	0.14743	0.16769
1.5	0.14272	0.15278	0.17479
2.0	0.14757	0.15635	0.18015
2.5	0.15234	0.15901	0.18535
3.0	0.15854	0.16269	0.19020
3.5	0.16237	0.16424	0.19145
4.0	0.17307	0.16505	0.19000
4.2	-	-	0.18925
4.5	0.17559	0.16508	-
4.6	-	-	0.18500
4.8	-	-	0.18066
5.0	0.18300	0.16386	0.17429
5.2	-	-	0.16160
5.4	-	-	0.12454
5.5	0.18336	0.16136	-0.17226

(Contd.)

T A B L E - 34(Contd.)

5.6	-	0.16100	0.28126
5.8	-	0.16013	0.29400
6.0	0.18415	0.15930	0.29470
6.2	-	0.15636	-
6.4	-	0.15249	-
6.5	0.18375	0.15112	-
6.6	-	0.14786	-
6.8	-	0.13505	-
7.0	0.18327	0.12068	0.29470
7.2	-	-0.15900	-
7.4	-	0.30800	-
7.5	0.18209	-0.31419	-
7.6	-	0.31419	-
7.8	-	0.31419	-
8.0	0.17966	0.36019	0.29470
8.5	0.17700	0.38947	-
9.0	0.17410	-	-
9.5	0.16724	0.38947	-
10.0	0.15407	0.38947	-
10.2	0.14364	-	-
10.4	0.09175	-	-
10.6	0.08164	-	-
11.0	-0.07300	-	-

(Contd.)

T A B L E - 34(Contd.)

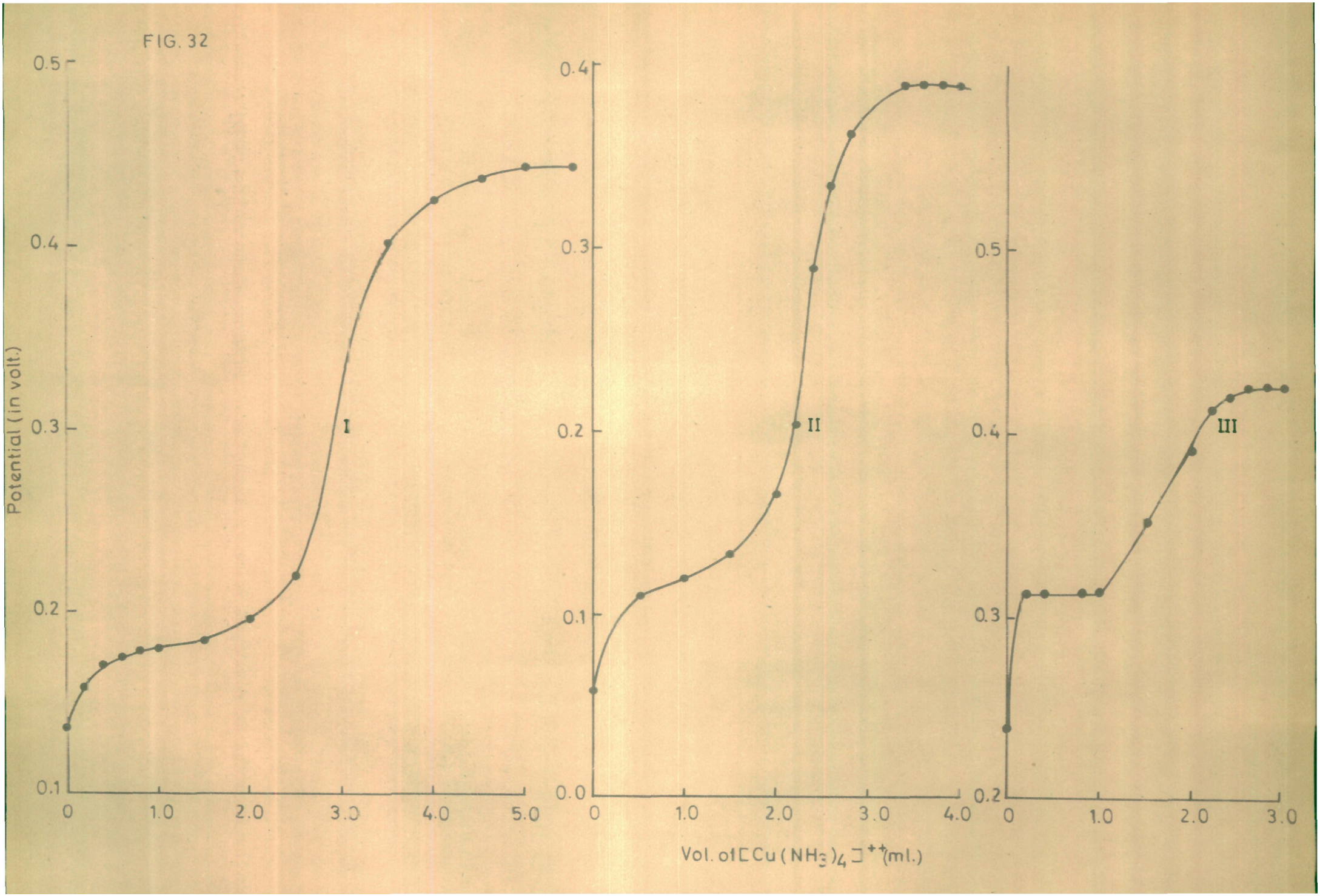
11.2	0.13000	-	-
11.6	0.15916	-	-
11.8	0.23116	-	-
12.0	0.25639	-	-
12.2	0.26539	-	-
12.7	0.27363	-	-
13.7	0.27200	-	-
14.0	0.27200	-	-
Fig.(31)	Curve(I)	Curve(II)	Curve(III)

Curve(I) : 20ml. of 2.5×10^{-2}M $\left[Cu(NH_3)_4\right]^{2+}$ = 11.0ml. of 2.5×10^{-2}M TCM

Curve(II) : 20ml. of 1.667×10^{-2}M $\left[Cu(NH_3)_4\right]^{2+}$ = 7.2ml. of 2.5×10^{-2}M "

Curve(III) : 20ml. of 1.25×10^{-2}M $\left[Cu(NH_3)_4\right]^{2+}$ = 5.5ml. of 2.5×10^{-2}M "

FIG. 32


Potential (in volt.)
0.5
0.4
0.3
0.2
0.1
0
1.0
2.0
3.0
4.0
5.0
I
0.4
0.3
0.2
0.1
0.0
0
1.0
2.0
3.0
4.0
II
0.5
0.4
0.3
0.2
0
1.0
2.0
3.0
III
Vol. of [Cu(NH3)4]++ (ml.)

T A B L E - 35.

Vol.of TCM = 20.0 ml.

Strength of $[Cu(NH_3)_4]^{2+}$ = 1.0×10^{-1}M.

Vol.of $[Cu(NH_3)_4]^{2+}$ added (ml.)	Potential (vs.S.C.E., volt)		
	TCM = 2.5×10^{-2}M	= 1.667×10^{-2}M	= 1.25×10^{-2}M
0.0	- 0.13800	- 0.05900	- 0.23900
0.2	0.15900	-	0.31300
0.4	0.17100	-	0.31300
0.5	-	0.11000	-
0.6	0.17500	-	0.30600
0.8	0.18000	-	0.31300
1.0	0.18000	0.12000	0.30600
1.5	0.18500	0.13400	0.35200
2.0	0.19710	0.16600	0.39000
2.2	-	0.20200	0.41300
2.4	-	0.28900	0.41900
2.5	0.22000	-	-
2.6	-	0.33200	0.42400
2.8	-	0.36100	0.42500
3.0	-	0.36600	0.42500

(Contd.)

T A B L E - 35(Contd.)

3.2	-	0.36600	-
3.4	-	0.38900	-
3.5	0.40200	-	-
3.6	-	0.38900	-
3.8	-	0.38900	-
4.0	0.42500	0.38900	-
4.5	0.43800	-	-
5.0	0.44300	-	-
Fig.(32)	Curve(I)	Curve(II)	Curve(III)

Curve(I) : 20ml.of 2.5×10^{-2}M TCM = 3.5ml.of 1.0×10^{-1}M $\left[Cu(NH_3)_4\right]^{2+}$

Curve(II) : 20ml.of 1.667×10^{-2}M TCM=2.6ml.of 1.0×10^{-1}M "

Curve(III): 20ml.of 1.25×10^{-2}M TCM =2.0ml.of 1.0×10^{-1}M "

FIG. 33

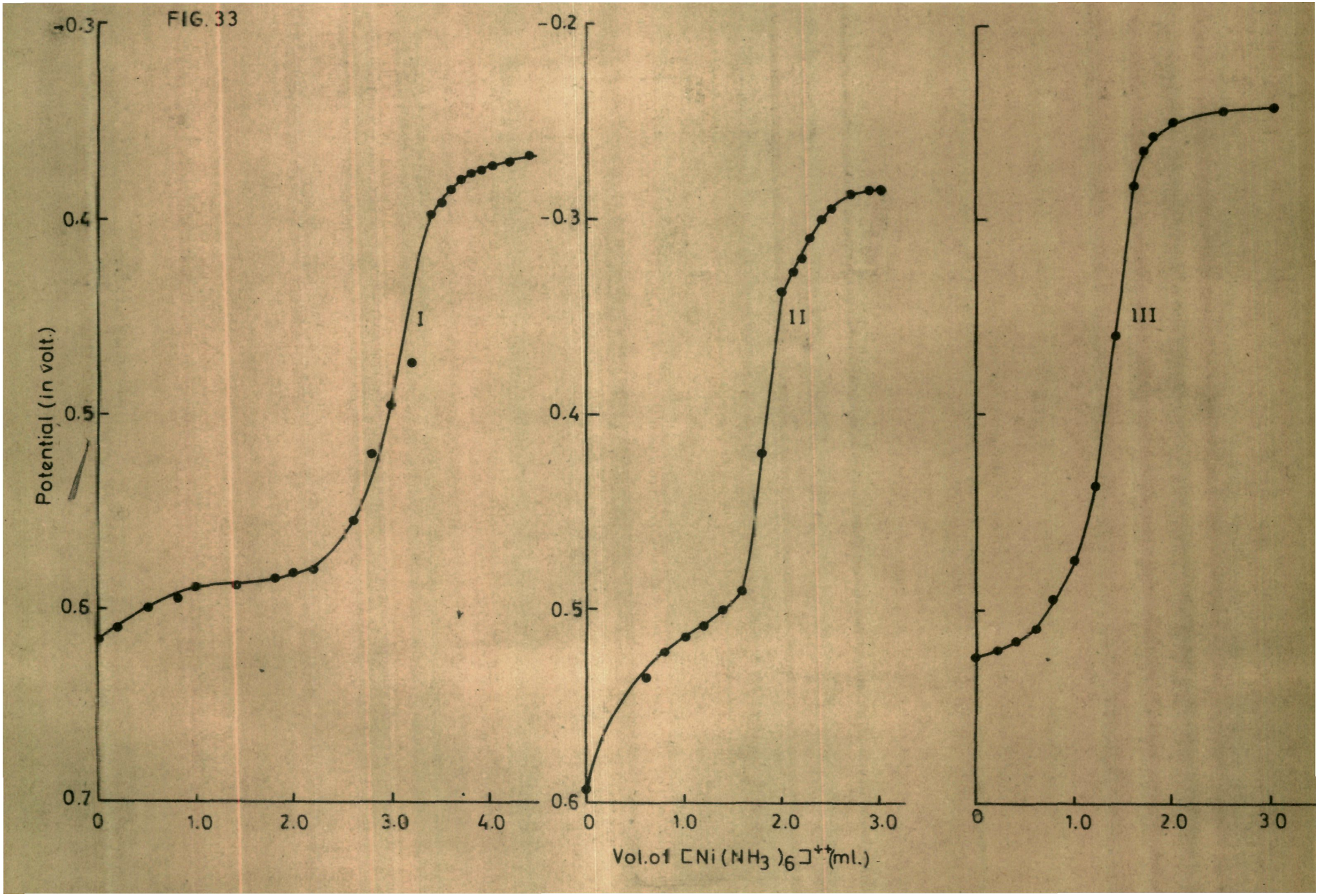

-0.3
0.4
0.5
0.6
0.7
Potential (in volt.)
0
1.0
2.0
3.0
4.0
I
-0.2
-0.3
0.4
0.5
0.6
0
1.0
2.0
3.0
II
Vol.of [Ni(NH3)6]++(ml.)
III
0
1.0
2.0
3.0

TABLE - 36.

Vol. of TCM = 20.0 ml.

Strength of $\left[Ni(NH_3)_6\right]^{2+}$ = 1.0×10^{-1}M

Vol.of $\left[Ni(NH_3)_6\right]^{2+}$ added(ml.)	Potential (vs.S.C.E. volt)		
	TCM=1.0×10^{-2}M	= 6.67×10^{-3}M	= 5.00×10^{-3}M
0.0	-0.61584	-0.59402	-0.52359
0.2	0.61050	-	0.52000
0.4	-	-	0.51801
0.5	0.60000	-	-
0.6	-	0.53900	0.51051
0.8	0.59500	0.52258	0.49751
1.0	0.56500	0.51500	0.47584
1.2	-	0.51012	0.43684
1.4	0.58900	0.50200	0.35957
1.6	-	0.49000	0.28236
1.8	0.58500	0.42500	0.25859
2.0	0.58300	0.32800	0.25159
2.2	0.58000	0.32100	-
2.3	-	0.31300	-
2.4	-	0.30000	-
2.5	-	0.29600	0.24559

(Contd.)

T A B L E -36(Contd.)

2.6	0.55400	-	-
2.7	-	0.28800	-
2.8	0.52000	-	-
2.9	-	0.28500	-
3.0	0.49500	0.28500	0.24359
3.2	0.47400	-	-
3.4	0.40400	-	-
3.5	0.39200	-	-
3.6	0.38500	-	-
3.7	0.38000	-	-
3.8	0.37700	-	-
3.9	0.37500	-	-
4.0	0.37300	-	-
Fig.(33)	Curve(I)	Curve(II)	Curve(III)

Curve(I) : 20ml.of 1.0×10^{-2}M TCM = 3.6ml.of 1×10^{-1}M $\left[Ni(NH_3)_6\right]^{2+}$

Curve(II) : 20ml.of 6.67×10^{-3}M TCM = 2.6ml.of 1×10^{-1}M "

Curve(III) : 20ml.of 5.0×10^{-3}M TCM = 1.8ml.of 1×10^{-1}M "

TABLE - 37.

Summary of the results of potentiometric titrations between potassium oxohydroxomolybdocyanide and silver ammine.

Direct: $\left[Ag(NH_3)_2\right]^+$ in the cell.

$\left[Ag(NH_3)_2\right]^+$ Vol. (ml.)	Concn.	Vol.of TCM soln. eqvt.to $\left[Ag(NH_3)_2\right]^+$ (ml.)	Ratio (TCM : Ag^+)
20	1.0×10^{-2}M	2.0	1 : 4
20	6.67×10^{-3}M	1.4	1 : 4
20	5.0×10^{-3}M	1.0	1 : 4

TABLE - 38.

Summary of the results of potentiometric titrations between potassium oxohydroxomolybdocyanide and copper ammine.

Direct: $[Cu(NH_3)_4]^{2+}$ in the cell.

$[Cu(NH_3)_4]^{2+}$ Vol. (ml.)	Concn. (10^{-2}M)	Vol.of TCM soln. eqvt. to $[Cu(NH_3)_4]^{2+}$ (ml.)	Ratio (TCM : Cu^{2+})
20	2.50	11.0	1 : 1.82
20	1.66	7.2	1 : 1.85
20	1.25	5.5	1 : 1.82

Reverse: TCM solution in the cell.

TCM solution Vol. (ml.)	Concn. (10^{-2}M)	Vol.of $[Cu(NH_3)_4]^{2+}$ eqvt. to TCM soln. (ml.)	Ratio (TCM : Cu^{2+})
20	2.50	3.5	1 : 0.70
20	1.66	2.6	1 : 0.78
20	1.25	2.0	1 : 0.80

TABLE - 39.

Summary of the results of potentiometric titrations between potassium oxohydroxomolybdocyanide and nickel ammine.

Reverse: TCM solution in the cell.

TCM solution Vol. (ml.)	Concn.	Vol. of $[Ni(NH_3)_6]^{2+}$ eqvt. to TCM soln. (ml.)	Ratio (TCM : Ni^{2+})
20	1.0×10^{-2}M	3.6	1 : 1.80
20	6.66×10^{-3}M	2.6	1 : 1.95
20	5.0×10^{-3}M	1.8	1 : 1.80

Conductometric Titrations

Cambridge conductivity bridge (no. L-350140) with a dip cell (cell constant = 1.30) was used for the conductance measurements. Both, direct (oxohydroxomolybdocyanide as the titrant) and reverse (metal ammine as the titrant) titrations were performed. The titrations of TCM with cobalt ammine and TCT with nickel and cobalt ammine were not successful.

All the measurements were carried out at room temperature. Purified nitrogen gas was bubbled after each addition of the titrant, this ensured a thorough mixing of the reactents.

The following tables records the observations of conductometric titrations.

FIG. 34

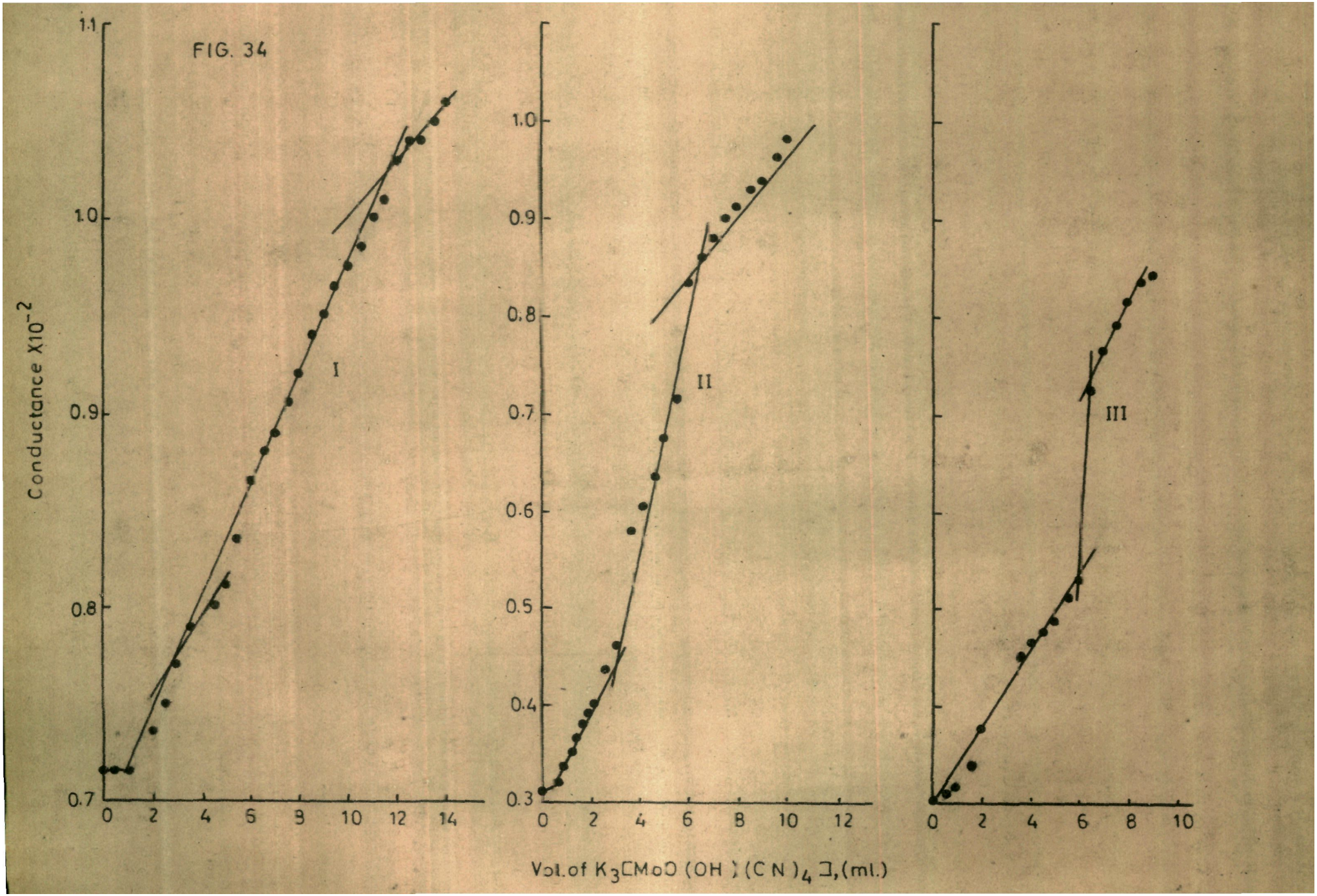

Conductance X10⁻²
1.1
1.0
0.9
0.8
0.7
I
0 2 4 6 8 10 12 14
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
II
0 2 4 6 8 10 12
III
0 2 4 6 8 10
Vol. of K3[MoO(OH)(CN)4], (ml.)

TABLE - 40.

Vol. of $[Cu(NH_3)_4]^{2+}$ = 20.0 ml.

Strength of TCM = 1.90×10^{-2} M

Vol. of TCM added (ml.)	Corrected Conductance X 10^{-2} (mhos)		
	$[Cu(NH_3)_4]^{++}$ = 2.50×10^{-2} M	= 1.67×10^{-2} M	= 1.25×10^{-2} M
0.0	0.715	0.310	0.300
0.2	-	0.310	0.300
0.4	-	0.310	0.300
0.6	0.715	0.320	0.310
0.8	-	0.335	0.310
1.0	0.715	0.340	0.315
1.5	0.715	0.370	0.325
2.0	0.735	0.400	0.375
2.5	0.750	0.435	0.430
3.0	0.770	0.460	0.450
3.5	0.790	0.580	0.455
4.0	0.800	0.605	0.465
4.5	0.810	0.635	0.475
5.0	0.81	0.675	0.485
5.5	0.835	0.715	0.510
6.0	0.865	0.835	0.530
6.5	0.880	0.860	0.725

(Contd.)

T A B L E - 40.(Contd.)

7.0	0.89	0.880	0.765
7.5	0.910	0.900	0.790
8.0	0.920	0.910	0.815
8.5	0.940	0.930	0.835
9.0	0.950	0.940	0.840
9.5	0.965	0.960	0.850
10.0	0.975	0.98	0.860
10.5	0.985	-	-
11.0	1.000	-	-
11.5	1.010	-	-
12.0	1.030	-	-
12.5	1.040	-	-
13.0	1.04	-	-
13.5	1.05	-	-
14.0	1.06	-	-
Fig.(34)	Curve(I)	Curve(II)	Curve(III)

Curve(I) : 20 ml.of 2.50×10^{-2}M $[Cu(NH_3)_4]^{++}$ = 12 ml.of 1.90×10^{-2}M TCM

Curve(II) : 20 ml.of 1.67×10^{-2}M $[Cu(NH_3)_4]^{++}$ = 9.0 ml.of 1.90×10^{-2}M "

Curve(III) : 20 ml.of 1.25×10^{-2}M $[Cu(NH_3)_4]^{++}$ = 6.0 ml.of 1.90×10^{-2}M "

FIG.35

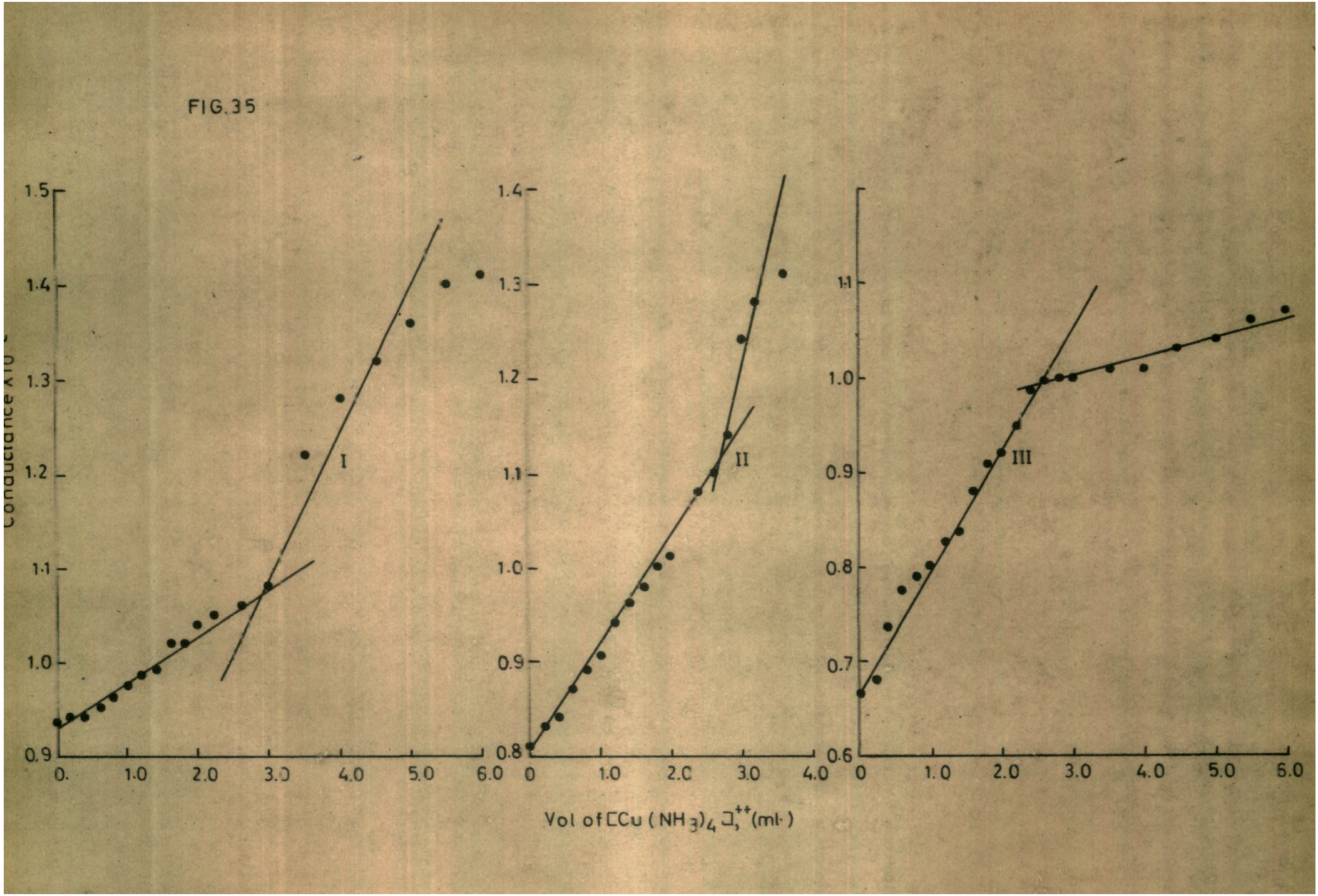

Conductance X10
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.
1.0
2.0
3.0
4.0
5.0
6.0
I
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0
1.0
2.0
3.0
4.0
II
1.1
1.0
0.9
0.8
0.7
0.6
0
1.0
2.0
3.0
4.0
5.0
III
Vol of [Cu(NH3)4]++ (ml.)

TABLE - 41.

Vol. of TCM = 20.0 ml.

Strength of $[Cu(NH_3)_4]^{2+}$ = 1.0×10^{-1} M.

Vol. of $[Cu(NH_3)_4]^{++}$ added (ml.)	Corrected Conductance X 10^{-2} (mhos.)		
	TCM = 1.90×10^{-2} M	= 1.67×10^{-2} M	= 1.25×10^{-2} M
0.0	0.935	0.810	0.660
0.2	0.940	0.830	0.680
0.4	0.940	0.840	0.735
0.6	0.950	0.870	0.770
0.8	0.960	0.890	0.790
1.0	0.975	0.905	0.800
1.2	0.985	0.94	0.825
1.4	0.990	0.960	0.835
1.6	1.020	0.980	0.880
1.8	1.020	1.000	0.910
2.0	1.040	1.010	0.920
2.2	1.050	1.010	0.950
2.4	1.050	1.080	0.985
2.6	1.060	1.100	0.990
2.8	1.060	1.140	1.000
3.0	1.080	1.240	1.000

(Contd.)

T A B L E - 41.(Contd.)

3.5	1.220	1.300	1.010
4.0	1.280	1.310	1.020
4.5	1.320	-	1.030
5.0	1.360	-	1.040
5.5	1.400	-	1.060
6.0	1.410	-	1.070
Fig.(35)	Curve(I)	Curve(II)	Curve(III)

Curve(I) : 20 ml.of 1.90×10^{-2}M TCM = 3.0 ml.of 1.0×10^{-1}M $[Cu(NH_3)_4]^{++}$

Curve(II) : 20 ml.of 1.67×10^{-2}M TCM = 2.6 ml.of 1.0×10^{-1}M "

Curve(III) : 20 ml.of 1.25×10^{-2}M TCM = 2.4 ml.of 1.0×10^{-1}M "

FIG-36

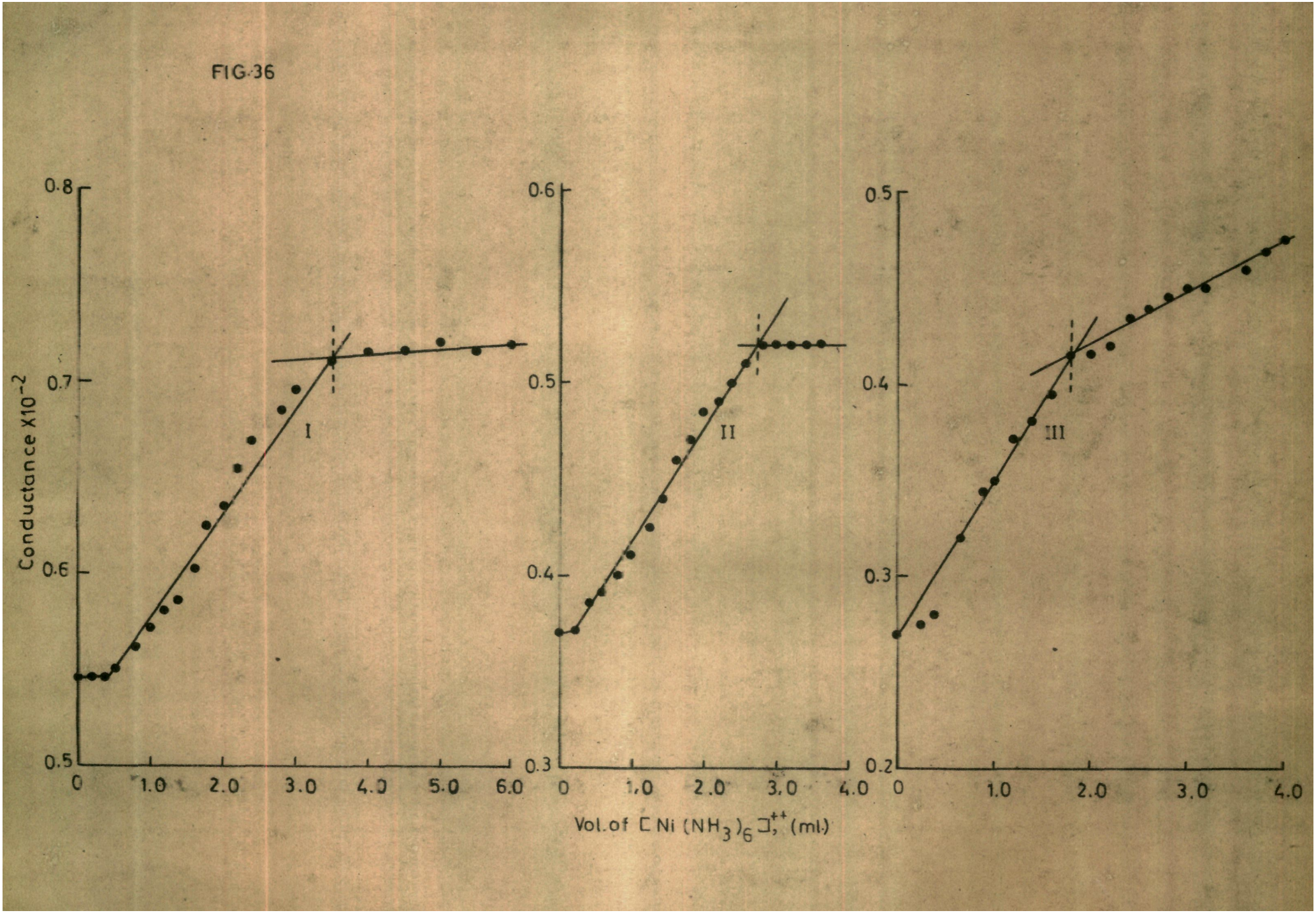

Conductance X10^{-2}
0.8
0.7
0.6
0.5
0
1.0
2.0
3.0
4.0
5.0
6.0
I
0.6
0.5
0.4
0.3
0
1.0
2.0
3.0
4.0
II
0.5
0.4
0.3
0.2
0
1.0
2.0
3.0
4.0
III
Vol. of [Ni $(NH_3)_6$]$^{++}$ (ml.)

TABLE - 42.

Vol.of TCM = 20.0 ml.

Strength of $[Ni(NH_3)_6]^{2+}$ = 1.0×10^{-1}M.

Vol.of $[Ni(NH_3)_6]^{++}$ added (ml.)	Corrected Conductance X 10^{-2}(mhos.) TCM = 1.0×10^{-2}M	= 6.67×10^{-3}	= 5.0×10^{-3}M
0.0	0.545	0.370	0.270
0.2	0.545	0.370	0.275
0.4	0.540	0.385	0.280
0.6	0.550	0.390	0.320
0.8	0.560	0.400	-
1.0	0.570	0.410	0.350
1.2	0.580	0.425	0.370
1.4	0.585	0.440	0.380
1.6	0.605	0.460	0.395
1.8	0.625	0.470	0.415
2.0	0.635	0.485	0.415
2.2	0.655	0.490	0.420
2.4	0.670	0.500	0.435
2.6	0.670	0.510	0.440
2.8	0.685	0.520	0.445
3.0	0.695	0.520	0.450

(Contd.)

T A B L E - 42.(Contd.)

3.2	-	0.520	0.450
3.4	-	0.520	0.460
3.6	-	0.525	0.460
3.8	-	0.540	0.470
4.0	0.715	0.550	0.505
4.5	0.715	-	-
5.0	0.720	-	-
5.5	0.715	-	-
6.0	0.720	-	-
Fig.(36)	Curve(I)	Curve(II)	Curve(III)

Curve(I) : 20 ml.of 1.0×10^{-2}M TCM = 3.5 ml.of 1.0×10^{-1}M $[Ni(NH_3)_6]^{++}$

Curve(II) : 20 ml.of 6.67×10^{-3}M TCM = 2.7 ml.of 1.0×10^{-1}M "

Curve(III) : 20 ml.of 5.0×10^{-3}M TCM = 2.0 ml.of 1.0×10^{-1}M "

T A B L E - 43.

Summary of the results of conductometric titrations between potassium oxohydroxomolybdocyanide and copper ammine.

Direct: $[Cu(NH_3)_4]^{2+}$ in the cell.

$[Cu(NH_3)_4]^{2+}$ Vol. (ml.)	Concn. (10^{-2}M)	Vol. of TCM soln. eqvt. to $[Cu(NH_3)_4]^{2+}$ (ml.)	Ratio (TCM : Cu^{2+})
20	2.50	12.0	1 : 2.16
20	1.67	9.0	1 : 1.95
20	1.25	6.0	1 : 2.19

Reverse: TCM solution in the cell.

TCM solution Vol. (ml.)	Concn. (10^{-2}M)	Vol. of $[Cu(NH_3)_4]^{2+}$ eqvt. to TCM Solution (ml.)	Ratio (TCM : Cu^{2+})
20	1.90	3.0	1 : 0.79
20	1.67	2.6	1 : 0.78
20	1.25	2.4	1 : 0.96

T A B L E - 44.

Summary of the results of conductometric titrations between potassium oxohydroxomolybdocyanide and nickel ammine.

Reverse: TCM solution in the cell.

TCM solution Vol. (ml.)	Concn.	Vol. of $[Ni(NH_3)_6]^{2+}$ eqvt. to TCM soln. (ml.)	Ratio (TCM : Ni^{2+})
20	$1x10^{-2}M$	3.5	1 : 1.77
20	$6.67x10^{-3}M$	2.7	1 : 2.00
20	$5x10^{-3}M$	2.0	1 : 2.00

D I S C U S S I O N

Reduction of silver ammine by tripotassium oxohydroxotetracyanomolybdate(IV)(TCM):

The results of potentiometric titrations between silver ammine and tripotassium oxohydroxotetracyanomolybdate(IV)(TCM) indicate that in the direct titrations i.e. when TCM was added to silver ammine, the two react in the ratio of 1:4 (Fig.30), with the formation of a soluble complex $Ag_2[Mo^{VI}O_2(CN)_4]$. The reaction seems to proceed as follows:

$$2[Ag(NH_3)_2]^+ + [Mo^{IV}O(OH)(CN)_4]^{3-} \longrightarrow [Mo^{VI}O(OH)(CN)_4]^{-1} + 2Ag + 4NH_3$$

$$2\,Ag(NH_3)_2^{+} + Mo^{VI}O(OH)(CN)_4^{-1} \longrightarrow Ag_2[Mo^{VI}O_2(CN)_4] + NH_4^+ + 3NH_3$$

The reverse titration does not give any break. Probably the reduction of silver ammine to Ag by TCM does not proceed in the absence of an alkali.

Reduction of copper ammine by tripotassium oxohydroxotetracyanomolybdate(IV)(TCM):

The results on potentiometric and conductometric titrations between TCM and copper ammine provide enough evidence regarding th composition of the complex formed. These titrations indicate the formation of complex 1:2 and 1:1 complexes during the direct and

the reverse titrations respectively. The following reaction may be visualized to take place:

$$\left[Cu(NH_3)_4\right]^{2+} + \left[Mo^{IV}O(OH)(CN)_4\right]^{3-} \longrightarrow \left[Mo^{VI}O(OH)(CN)_4\right]^{-1} + Cu + 4NH_3 \quad ..(1)$$

$$\left[Cu(NH_3)_4\right]^{2+} + \left[Mo^{VI}O(OH)(CN)_4\right]^{-1} \longrightarrow Cu\left[Mo^{VI}O_2(CN)_4\right] + NH_4^+ + 3NH_3 \quad ..(2)$$

The direct potentiometric as well as conductometric titrations (Figs.31 & 34) shows that the product formed in the ratio of 1:1 reaction(1) is unstable in the presence of excess of ammine and reacts with another molecule of copper ammine and ends up in a 1:2 instead of 1:1 complex. On the other hand in the reverse titrations the product formed according to the reaction (1) seems to be stable in the presence of TCM and hence the titrations indicates an end point of 1:1 (Figs.32 & 35).

A survey of the summarized results (Tables 38 & 43) would reveal the combining ratio 1:2 and 1:1 for ($TCM:Cu^{2+}$) in direct and reverse titrations respectively.

In conductometric titrations after the equivalence point (1:2), there is also regular increase in conductance. In direct conductometric titrations when TCM was added, two breaks are prominent, though the first one is not as sharp as the second. The first break corresponds to 1:1 for($TCM:Cu^{2+}$)and the second to corresponds to the ratio of 1:2 for ($TCM:Cu^{2+}$).

Reduction of Nickel ammine by tripotassium oxohydroxotetra - cyanomolybdate(IV)(TCM):

In the conductometric and potentiometric titrations of TCM and nickel ammine, only reverse titrations i.e. Ni ammine added to TCM were successful. In conductometric titrations when nickel ammine are added to TCM solution a regular increase in conductance before the equivalence point takes place (Fig.36). The reaction between TCM and nickel ammine may be represented by the following stoichiometric equations:

$$[Ni(NH_3)_6]^{2+} + [Mo^{IV}O(OH)(CN)_4]^{3-} \longrightarrow [Mo^{VI}O(OH)(CN)_4]^{-1} + Ni + 6NH_3 \quad ...(1)$$

$$[Ni(NH_3)_6]^{2+} + [Mo^{VI}O(OH)(CN)_4]^{-1} \longrightarrow Ni[MoO_2(CN)_4] + NH_4^+ + 5NH_3 \quad ... (2)$$

$$2[Ni(NH_3)_6]^{2+} + [Mo^{IV}O(OH)(CN)_4]^{3-} \longrightarrow Ni[Mo^{VI}O_2(CN)_4] + Ni + NH_4^+ + 11NH_3 \quad ..(3)$$

The results of conductometry were also confirmed by potentiometric titrations of varying concentrations of TCM (Fig.33). The ratio of (TCM:Ni^{2+}) comes out to be 1:2 (Table 44).

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1. K.N. Mikhalevich and V.N. Litvinchuk,
Zh. Neorgan Khim., 9 (10)(1964) 2391.

ACID DISSOCIATION CONSTANTS OF TETRACYANOHYDROXOOXOMOLYBDATE(IV) ION

By M. Aijaz Beg,* Kabir-ud-Din,* and R. A. Khan*

[Manuscript received 27 June 1972]

Abstract

The third dissociation constant of tetracyanohydroxooxomolybdic acid, $H_3[MoO(OH)(CN)_4]$, has been obtained in the temperature range 25–50°C from the pH–titration curve of its tripotassium salt against hydrochloric acid. The values of pK_3 fitted an equation of Harned–Robinson type:

$$pK_3 = (1730{\cdot}72/T) - 6{\cdot}19 + 0{\cdot}0308T$$

obtained by the method of least squares.

Thermodynamic quantities ΔG°, ΔH°, ΔS°, and ΔC_p° for the process have been evaluated at 30°C.

The interaction of tetracyanohydroxooxomolybdate(IV) ion with simple as well as complex metal ions,[1,2] its oxidation–reduction properties,[3] and reduction at a dropping mercury electrode[4] have been reported earlier. This communication deals with the determination of thermodynamic dissociation constants of this anion and the related thermodynamic quantities.

Experimental

Blue $K_3[MoO(OH)(CN)_4]$ was prepared by Jakob's[5] method as modified and reported earlier.[1–3] Its solution strength was determined potentiometrically by titrating against potassium hexacyanoferrate(III).[3]

Determination of Dissociation Constants

The acid dissociation constants were determined from acidimetric titration curves. Aqueous solutions (0·02M) of tripotassium tetracyanohydroxooxomolybdate(IV) were titrated with 0·1M aqueous hydrochloric acid and the concomitant change in the pH was read with a Beckman G pH-meter using glass (Beckman 40485) and calomel (Beckman 39970) electrodes. The pH-meter was calibrated with reference to a 0·05M potassium hydrogen phthalate solution which has pH values known at several temperatures.[6] Ionic strengths were maintained by adding appropriate concentrations of potassium chloride.

A typical titration curve (at 30°C) is given in Figure 1. It shows two inflection points corresponding to the addition of 1 and approx. 3 equiv. of H^+ per mole of the complex. The apparent equilibrium constants (pK_3') were obtained from the half-equivalence points of the first segment.

* Department of Chemistry, Aligarh Muslim University, Aligarh, U.P., India.

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[2] Kabir-ud-Din, Khan, A. A., and Beg, M. A., *J. electroanal. Chem.*, 1968, **19**, 175.
[3] Beg, M. A., Khan, A. A., and Kabir-ud-Din, *J. electroanal. Chem.*, 1968, **18**, 187.
[4] Beg, M. A., Kabir-ud-Din, and Khan, R. A., *J. inorg. nucl. Chem.*, in press.
[5] Jakob, Z., *Roczn. Chem.*, 1957, **31**, 681.
[6] Kaye, G. W. C., and Laby, T. H., "Physical and Chemical Constants," 12th Edn, p. 148 (Longmans: London 1959).

Materials

Reagent grade chemicals were used throughout. Doubly distilled water served as the solvent. To obviate oxidation, experiments were carried out in a nitrogen atmosphere. Prior to use nitrogen was purified by bubbling through chromous chloride and alkaline pyrogallol solutions and equilibrated with the solvent. Experiments were performed at constant temperature.

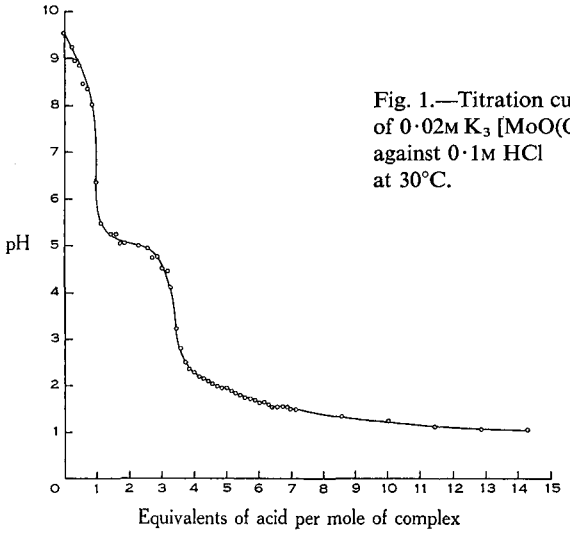

Fig. 1.—Titration curve of 0·02M K_3 [MoO(OH)(CN)$_4$] against 0·1M HCl at 30°C.

Results and Discussion

Potentiometric titrations of tripotassium tetracyanohydroxooxomolybdate(IV) with hydrochloric acid showed two inflection points. The first inflection occurs at a pH between 6·65 to 7·5. This corresponds to the formation of dibasic complex $[Mo(OH)_2(CN)_4]^{2-}$ due to the addition of one proton (H^+) to the predominating species $[MoO(OH)(CN)_4]^{3-}$. The pH at the mid-point of first segment is taken to be equal to pK_3'.

The equivalence points were determined from the derivative plot $\Delta pH/\Delta V$. The half-equivalence points in the titrations were then calculated and the pH values were found at these points. The pK_3' values obtained from several independent measurements lie within $\pm 0{\cdot}15$ ($\pm 0{\cdot}25$ at 30° and $\mu = 0{\cdot}4$).

When 3 equiv. of H^+ were added a second inflection point was obtained. Addition of more acid followed the appearance of a green gel-like precipitate, which on the addition of more acid, disappeared. Thus, at the end of titration (*c.* 15 equiv. of H^+) the solution was clear and its colour was brownish-green.

These reactions may be explained on the basis of formation of a colloidal solution (green) of the basic molybdenum cyanide. Coagulation occurs after some time and a green precipitate separates out. This substance is a product of the breakdown of the dibasic complex in accordance with the reaction:

$$[Mo(OH)_2(CN)_4]^{2-} + 2H^+ \rightarrow 2HCN + Mo(OH)_2(CN)_2 \text{ (green precipitate)}$$

This basic cyanide dissolves slowly in excess of the acid:

$$Mo(OH)_2(CN)_2 + 2H^+ \rightarrow 2HCN + MoO^{2+} + H_2O$$

A similar sequence of reactions has been proposed for the analogous tungsten compound.[7] The compound $Mo(OH)_2(CN)_2$ had been prepared earlier[8] and its sulphur derivative, $MoS(CN)_2$, is also known.[9]

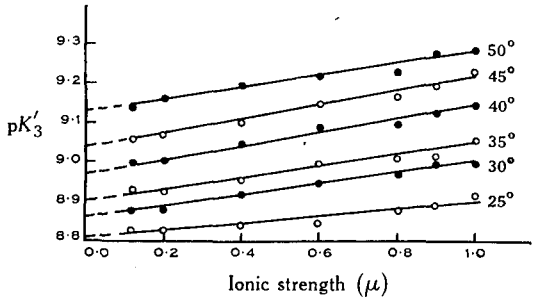

Fig. 2.—Extrapolation to zero ionic strength of pK_3' values observed at different temperatures.

The acid pK_3' at 16° has been calculated from hydrolysis studies to be 8·74.[7] This value has been determined by us for a wide range of temperature and ionic strength, in good agreement with the value reported from hydrolysis data. We have also determined the thermodynamic constants at different temperatures from extrapolation of pK_3' values against the corresponding ionic strength, μ (Fig. 2). Values obtained from extrapolation are:

Temp. (°C)	25	30	35	40	45	50
pK_3	8·81	8·86	8·90	8·97	9·04	9·13

The variation of pK_3 with temperature is given by a Harned–Robinson equation:[10]

$$pK_3 = A^*/T - D^* + C^*T \qquad (1)$$

The pK_3 data were treated (by use of a computer) by a least-squares method in which the fit of the data to a wide range of sets of possible values could be tested and the significance of any particular value assessed. The program was run on an IBM 1130 computer. The following equation was obtained:

$$pK_3 = (1730{\cdot}72/T) - 6{\cdot}19 + 0{\cdot}0308T \qquad (2)$$

The maximum deviations in pK_3 values obtained from this equation, and those found experimentally, lie within $\pm 0{\cdot}02$ unit. Thermodynamic quantities at 30° derived from this equation[11] are ΔG° +12264 cal mol^{-1}, ΔH° −5016 cal mol^{-1}, ΔS° −57 cal K^{-1} mol^{-1}, ΔC_p° −85 cal K^{-1} mol^{-1}.

Acknowledgment

The authors are grateful to Professor Wasiur Rahman for providing research facilities.

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J. Inorg. Nucl. Chem. 35 (1973) 2801

Polarographic study of oxo-hydroxo-cyanomolybdate(IV) ion:-

M.Aijaz Beg, Kabir-ud-Din and Rais A. Khan
Chemistry Department, Aligarh Muslim University, Aligarh, U.P., India.

Abstract:- The polarographic behaviour of tripotassium oxo-hydroxo-cyanomolybdate(IV), $K_3[Mo^{IV}O(OH)(CN)_4].2H_2O$ was studied. The complex was found to be oxidised step-by-step to the $Mo^{(VI)}$ state at the dropping mercury electrode in an aqueous solution which contains 0.1M KNO_3 and 0.01% gelatin. The resulting molybdate(VI) complex is presumed to be hexa-co-ordinated $[Mo^{VI}O(OH)(CN)_4]^{1-}$ like the original molybdate(IV) complex, and the electrode process can be given as:

$$[Mo^{IV}O(OH)(CN)_4]^{3-} \xrightarrow{e} [Mo^{V}O(OH)(CN)_4]^{2-} \xrightarrow{e} [Mo^{VI}O(OH)(CN)_4]^{-1}$$

I N T R O D U C T I O N

The crystalline potassium hydroxocyanomolybdate(IV) was obtained by Pechard in 1894[1]. The properties of this compound, and other molybdocyanides and their derivatives, have been studied by a number of investigation[2-11] since that time. Most investigators have favoured the eight-co-ordinate formulations, $[Mo(OH)_4(CN)_4]^{4-}$ (red) and $[Mo(OH)_3(OH)_2(CN)_4]^{3-}$(blue), but the recent crystallographic work[12-15] has shown that these compounds are best formulated as six-co-ordinate $[MoO_2(CN)_4]^{4-}$ and $[MoO(OH)(CN)_4]^{3-}$, respectively.

No mention is made in the existing chemical literature of the polarographic study of these tetracyano complexes of molybdenum(IV). The only polarographic work done on octacyanomolybdates(IV,V)[16].

This communication deals with the polarographic study of the blue hydroxo-cyanomolybdate(IV) ion, $[Mo^{IV}O(OH)(CN)_4]^{3-}$.

EXPERIMENTAL

Materials: Tripotassium oxohydroxocyanomolybdate(IV) dihydrate was prepared as described earlier[10]. Its solution strength was determined potentiometrically by titrating with standard potassium hexacyanoferrate(III)[10]. All other chemicals used were of guaranteed reagent grade.

Apparatus:- A manual polarograph manufactured by Toshniwal Brothers, New Delhi, India (Type CL02A) in conjunction with Toshniwal spot galvanometer (Cat.No.PL64.01) was used to obtain d.c. polarograms. The reference electrode was a saturated calomel electrode. A side tube from the reference electrode with porous end plate, filled with KNO_3 (satd.) agar, was used to connect the two halves of the cell. The cell and the reference electrode were kept in a water thermostat . The capillary characteristic were m = 1.778 mg/sec., t = 4.62 sec.(measured in water at an open circuit) with a mercury head of 81.25 cm.

Prior to analysis each polarographic solution was deoxygenated by a stream of nitrogen which had been passed successively through chromous chloride and alkaline pyrogallol solutions.

RESULTS AND DISCUSSION

Evaluation of Kinetic parameters:

The oxohydroxocyanomolybdate(IV) ion; $Mo^{IV}O(OH)(CN)_4^{3-}$, gave rise to two step oxidation wave in 0.1M KNO_3 aqueous solution at DME. The first step is reversible while the second step is irreversible. The apparent kinetic parameters for the second step oxidation process have been determined by Koutecky's[17] method, as advanced by Meites and Israel[18]. Polarogram of a solution containing 1.0mM complex in 0.1M KNO_3 and 0.01% gelatin was taken at 25°C. In this case the current at the end of drop life was recorded instead of average current, because the kinetic parameters are more accurately reproduced by measuring the maximum current. The value of t were measured at different potentials on the rising portion of the wave, such that i lies between the 10 and 90 percent i_d, which are the approximate limits of the validity of the equation employed in the calculations.

For an anodic wave the equation is given as:

$$E_{d.e.} + 0.2412 = -\frac{0.05915}{\beta n}\log\frac{1.349\,k^{o}_{b,h}}{D^{\frac{1}{2}}} + \frac{0.0542}{\beta n}\left[\log\frac{i_d - i - 0.546\log t}{I}\right] \quad \ldots\ldots\ldots (1)$$

and

$$E^{o}_{\frac{1}{2}} = -0.2412 - \frac{0.05915}{\beta n}\log\frac{1.349\,k^{o}_{b,h}}{D^{\frac{1}{2}}} \quad \ldots\ldots (2)$$

where the terms have their usual significance.

The kinetic parameters have been calculated employing equations (1) and (2). The values of βn was obtained by equating the slope 0.075 of the straight line plot, $E_{d.e.}$ versus

$$\left[\log \frac{i_d - i}{i} - 0.0546 \log t\right]$$

with 0.0542/βn. The same plot gave the intercept $E_{\frac{1}{2}}^{o} = 0.295V$ which was used to calculate $k_{b,h}^{o}$ employing equation(2). The value of $k_{b,h}^{o}$ was calculated by means of the equation:

$$k_{b,h} = k_{b,h}^{o} \exp\left[\frac{\beta nF}{RT}\left(E + 0.2412\right)\right] \qquad \ldots\ldots \quad (3)$$

Diffusion coefficient was obtained by means of Ilkovic equation taking n = 1. The value of $k_{b,h}^{o}$ was calculated at E = - 0.33V, the half wave potential of the second wave.

The oxohydroxocyanomolybdate(IV) ion, $\left[Mo^{IV}O(OH)(CN)_4\right]^{3-}$ gave rise to two step oxidation wave in a 0.1M KNO_3 aqueous solution at the DME.

Conventional log plot showed that the first step ($E_{\frac{1}{2}}$ = - 0.09V vs SCE.) is reversible corresponding to a loss of one electron while the following second step ($E_{\frac{1}{2}}$ = - 0.33V vs.S.C.E.) is irreversible. The apparent kinetic parameters for this second step oxidation process have been evaluated by applying Koutecky's[17] theoretical treatment as extended by Meites and Israel[18] and summarized in table 1.

TABLE -1. Apparent kinetic parameters of the electrode process for the $K_3[Mo^{IV}O(OH)(CN)_4].2H_2O$ complex in a 0.1M KNO_3 and 0.01% gelatin solution:

i_d (μA)	$Dx10^6$ (cm^2sec^{-1})	βn	$k^o_{b,h} \times 10^3$ ($cm.sec^{-1}$)	log $k_{b,h}$	$k_{b,h} \times 10^4$ ($cm.sec^{-1}$)
3.16_3	3.34_4	0.72_2	6.15_6	-3.29_6	5.06_0

Diffusion currents for each waves were proportional to the concentration of the depolarizer in the range 0.5-3.0mM and constant values of i_d/C and t were found. Thus potassium oxohydroxocyanomolybdate(IV) can be estimated quantitatively in the range 0.5-3.0mM taking into consideration either of the two waves. The half potentials of both the waves were found to be independent of depolarizer concentration.

The diffusion currents of the first as well as the second step were found to be proportional to the square root of the mercury pressure on the DME, the values of $i_d/h^{\frac{1}{2}}_{corr.}$ were constant, irrespective of the mercury pressure.

The temperature dependence of diffusion currents of both the waves were studied in the range of 25-50C° at intervals of 5°C. Above 35°C, the current values were found to deviate from straight lines of plot; the current increases remarkedly with the temperature, indicating a kinetically-controlled feature.

This may be attributed to the probable disruption of the Mo(IV) complex in solution. Below 35°C, the current changes of both the waves were linear with temperature; the coefficient being 1.3 and 1.6%/degree respectively at 25°C. On the whole, no deformation of the waves with temperature were observed.

The linearity of i_d with depolarizer concentration, $h^{\frac{1}{2}}_{corr.}$ and temperature and the values of temperature coefficients of i_d are in accord with the anodic limiting currents being controlled totally by diffusion upto 35°C.

Electrode reaction:-

As the value of βn found is 0.72, n = 1.4 with β = 0.5 which must be an integer. Thus one would conclude that n = 1. This values has further been checked by plotting the first derivative polarogram $\Delta i/\Delta E$ vs.E which shows only one peak. With this value of n, the second step reaction can be presumed to be:

$$\left[Mo^{V}O(OH)(CN)_4\right]^{2-} \longrightarrow \left[Mo^{VI}O(OH)(CN)_4\right]^{1-} + e.$$

Thus the overall electrode reaction may be described as:

$$\left[Mo^{IV}O(OH)(CN)_4\right]^{3-} \xrightarrow{e} Mo^{V}O(OH)(CN)_4{}^{2-} \xrightarrow{e} \left[Mo^{VI}O(OH)(CN)_4\right]^{1-}$$

in which no chemical reaction seems to be appreciably involved at this temperature.

Acknowledgement:- The authors are thankful to Professor Wasiur Rahman, Head Department of Chemistry, for providing research facilities.

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Z. Physik. Chem. (in press)

POLAROGRAPHIC STUDY OF TRANS-DIOXOTETRACYANOTUNGSTATE(IV) ION

M. ALJAZ BEG, KABIR-UD-DIN AND RAIS A. KHAN
Department of Chemistry, Aligarh Muslim University, Aligarh, India
(Received August 22, 1973 and accepted)

The polarographic behaviour of tetrapotassium dioxotetracyanotungstate(IV), $K_4[W^{IV}O_2(CN)_4] \cdot 6H_2O$ at dropping mercury electrode has been investigated in aqueous medium in the presence of 0.1M KIO_3 and 0.01% gelatin.

The complex was found to be oxidized step-to-step to the tungstate(VI) state. The resulting tungstate(VI) complex is presumed to be hexa-coordinated trans-$[W^{VI}O_2(CN)_4]^{4-}$ like the original tungstate(IV) complex, and the electrode process can be given as:

$$[W^{IV}O_2(CN)_4]^{4-} \xrightarrow{e} [W^{V}O_2(CN)_4]^{3-} \xrightarrow{e} [W^{VI}O_2(CN)_4]^{2-}$$

The crystalline potassium hydroxocyanotungstate(IV) was first obtained by COLLENBERG[1] who assigned the formula $K_4[W(OH)_3(CN)_5] \cdot 6H_2O$. The properties of this compound and other hydroxotungstocyanides have been studied by a number of investigators[2-7] and the recent crystallographic work[6,7] has established that the hydroxocyanides are best formulated as six coordinate oxocyanides instead of previous eight coordinate

formulations.[3] The compound $K_4[WO_2(CN)_4].6H_2O$ is shown to have two oxygen atoms trans to each other.

There is no reference in the literature regarding the polarographic behaviour of oxotetracyanide complexes of tungsten. The only polarographic work done is on octacyanotungstates(IV,V).[8,9] This communication deals with the electrochemical behaviour of the trans- dioxotetracyanotungstate(IV) ion, $[WO_2(CN)_4]^{4-}$, at d.m.e. carried out on the similar lines to that for oxohydroxocyanomolybdate(IV)[10] ion.

EXPERIMENTAL

Materials

Tetrapotassium dioxotetracyanotungstate(IV) hexahydrate, $K_4[WO_2(CN)_4].6H_2O$, was prepared and standardized as described earlier.[5] All other chemicals used were of guaranteed reagent-grade.

Apparatus

D.C. polarograms were obtained using a Fischer Elecdropode. The details of reference electrode (SCE) used are described elsewhere.[10] Triple distilled mercury was used in dme. and capillary characteristic were m = 1.411 mg/sec; t = 3.89 sec. (measured in water at an open circuit) at h=43.0 cm. and 0°C. Potassium nitrate

(0.1M) was used as the base electrolyte and gelatin (0.01%) as the maximum suppressor.

Prior to analysis, each test solution was deoxygenated by a stream of nitrogen gas which has previously been passed successively through chromous chloride and alkaline pyrogallol solutions.

RESULTS AND DISCUSSION

The dioxotetracyanotungstate(IV) ion, trans $\left[WO_2(CN)_4\right]^{4-}$, produces two anodic waves in a 0.1M KNO_3 aqueous solution at the dme (Fig.1). Conventional log plots (Fig.2) showed that the first step oxidation ($E_{\frac{1}{2}}$ = 0.195V vs.SCE) is irreversible (slope = 0.09) while the following second step oxidation ($E_{\frac{1}{2}}$ = - 0.435V vs.SCE) is reversible (slope = 0.055) corresponding to a loss of one electron. The apparent kinetic parameters for the first step oxidation process have been evaluated by applying KOUTECKY's[11] theoretical treatment as extended by MEITES and ISRAEL.[12]

The effect of variation of depolarizer concentration, drop-time and temperature was studied to establish the characteristics of the waves.

Effect of depolarizer concentration

Polarograms of the depolarizer ranging from 6.05mM to 17.50mM were taken. Diffusion Currents for each wave were proportional to the concentration and almost constant values of id/C and diffusion current constant ($I = id/C\, m^{2/3} t^{1/6}$) were found. The relation between the diffusion currents and concentrations (Figs.3 and 4, Curve I) shows that both the lines pass through origin. Thus, potassium dioxotetracyanotungstate(IV) can be estimated quantitatively taking into consideration either of the waves.

The half-wave potentials of both the waves were found to be independent of depolarizer concentration.

Effect of Hg-pressure

The diffusion currents of the first as well as the second step were found to be proportional to the square-root of the heights of mercury column on dme, the values of $id/h^{\frac{1}{2}}_{corr.}$ were constant, irrespective of the mercury pressure (Table 1). This shows that height of both the anodic waves is solely controlled by the diffusion factor. Fig.3 and 4 (Curves II) show the dependence of the diffusion currents on mercury pressure for a solution containing 14.60mM $[WO_2(CN)_4]^{4-}$ in 0.1M KNO_3 and 0.01% gelatin.

TABLE - 1. Effect of mercury pressure.

$\left[MO_2(CN)_4\right]^{4-}$ = 14.6mM, KNO_3 = 0.1M, gelatin = 0.01% (0°C)

h_{Hg} (cm)	m (mg/sec)	t (sec)	mt (mg)	$h_{corr.}$ (cm)	$h^{\frac{1}{2}}_{corr.}$ ($cm^{\frac{1}{2}}$)	$100m/h_{corr.}$	$h_{corr}t.$	i_d' (uA)	i_d'' (uA)	$i_d'/h^{\frac{1}{2}}_{corr.}$	$i_d''/h^{\frac{1}{2}}_{corr.}$
40.0	1.331	4.12	5.524	38.24	6.184	34.80	157.6	6.58_3	5.72_8	1.064	0.926
43.0	1.411	3.89	5.485	41.24	6.421	34.22	160.4	6.66_9	5.89_9	1.039	0.918
45.0	1.481	3.70	5.480	43.24	6.575	34.26	160.0	6.84_0	6.070	1.040	1.923
50.0	1.639	3.35	5.491	48.24	6.945	33.98	161.5	7.35_3	6.41_2	1.059	0.923
55.0	1.829	3.00	5.487	53.24	7.295	34.37	159.7	7.59_5	6.84_0	1.054	0.937
60.0	1.992	2.75	5.478	58.24	7.632	34.19	160.2	8.20_8	7.09_6	1.075	0.929
Means	-	-	5.490_8	-	-	34.30_3	159.9	-	-	1.031	0.926

Back pressure = $3.1/(mt)^{1/3}$ = $3.1/(5.49)^{1/3}$ = 1.76 cm. of Hg.

Effect of temperature

A series of polarograms of 6.0% complex were drawn at different temperatures ranging from 0 to 25°C at intervals of 5°. Figs.3 and 4 (Curves III) show the temperature dependence of the diffusion currents. Above 10°C, the current values were seen to deviate from the straight lines of the plot; the current increases remarkedly with the temperature, indicating a kinetically-controlled feature. This may be attributed to the probable distruption of the final complex formed in solution. Below 10°C, the current changes of both the waves were linear with temperature. The values of temperature coefficients of diffusion currents for each temperature interval were calculated employing ILKOVIC's[13] method. The mean values for first and second waves were found as 0.529 and 0.965%/degree respectively at 0°C.

The linearity of id with depolarizer concentration, $h^{\frac{1}{2}}_{corr.}$ and temperature and the values of temperature coefficients of id are in accord with the anodic limiting currents being controlled totally by diffusion upto 10°C.

Evaluation of kinetic parameters

Table 2 summarizes the apparent kinetic parameters for the irreversible first step oxidation process. These parameters

have been determined by KOUTECKY's[11] method as advanced by MEITES and ISRAEL.[12] Polarogram of a solution containing 6.05mM complex in 0.1M KNO_3 and 0.01% gelatin was taken at 0°C (Fig.5, Curve I). In this case the current at the end of the drop-life was recorded instead of average current, because the kinetic parameters are more accurately reproduced by measuring the maximum current. The values of t were determined at different potentials on the rising portion of the wave, such that i lies between 10 to 95% i_d, which are the approximate limits of the validity of the equation employed in the calculations.

For a cathodic wave the equation at 25°C is given as:[12]

$$E_{d.e} + 0.2412 = \frac{0.05915}{\alpha n} \log \frac{1.349\, k^{o}_{f,h}}{D^{\frac{1}{2}}} - \frac{0.0542}{\alpha n}\left[\log \frac{1}{i_d - i} - 0.546 \log t\right] \quad \ldots\ldots \quad (1)$$

where the terms have their usual significance.[14] To obtain an identical equation for anodic wave, αn is replaced by $-(1-\alpha)_n = -\beta_n$ and $k^{o}_{f,h}$ by $k^{o}_{b,h}$, then

$$E_{d.e.} + 0.2412 = -\frac{0.05915}{\beta n} \log \frac{1.349\, k^{o}_{b,h}}{D^{\frac{1}{2}}} + \frac{0.0542}{\beta n}\left[\log \frac{i_d - i}{i} - 0.546 \log t\right] \quad \ldots\ldots \quad (2)$$

At 0°C, equation (2) will become

$$E_{d.e.} + 0.2602 = - \frac{0.5419}{\beta n} \log \frac{1.349\, k^{o}_{b,h}}{D^{\frac{2}{3}}} + \frac{0.0497}{\beta n}\left[\log \frac{i_d - i}{i} - 0.545 \log t\right] \quad \ldots\ldots \quad (3)$$

by using 0.2602 volt as the potential of saturated calomel electrode at 0°C.[15]

$$E_{d.e.} = E^{o}_{\frac{1}{2}} + \frac{0.0497}{\beta n}\left[\log \frac{i_d - i}{i} - 0.545 \log t\right] \quad \ldots\ldots \quad (4)$$

where

$$E^{o}_{\frac{1}{2}} = - 0.2602 - \frac{0.05419}{\beta n} \log \frac{1.349\, k^{o}_{b,h}}{D^{\frac{2}{3}}} \quad \ldots\ldots \quad (5)$$

The kinetic parameters have been calculated employing equations(4) and (5). The value βn was obtained by equating the slope 0.083 of the straight line plot $E_{d.e.}$ versus

$$\left[\log \frac{i_d - i}{i} - 0.545 \log t\right]$$

(Fig.5, Curve II) $0.0497/\beta n$. The same plot gave the intercept $E^{o}_{\frac{1}{2}} = - 0.225V$ which was used to calculate $k^{o}_{b,h}$, employing eq.(5). The value of $k_{b,h}$ was calculated by means of the equation

$$k_{b,h} = k^{o}_{b,h} \exp\left[\frac{\beta nF}{RT}(E + 0.2602)\right]. \quad \ldots\ldots \quad (6)$$

Diffusion coefficient was obtained by means of the ILKOVIC equation taking n=1. The value of $k_{b,h}$ was calculated at E = - 0.435V, the half-wave potential of the second wave.

Table 2. Apparent kinetic parameters of the electrode process for the $K_4[WO_2(CN)_4] \cdot 6H_2O$ complex in a 0.1M KNO_3 and 0.01% gelatin solution (°C).

i_d (μA)	$Dx10^7$ (cm^2sec^{-1})	βn	$k^o_{b,h}x10^4$ ($cm.sec^{-1}$)	log $k_{b,h}$	$k_{b,h}x10^5$ ($cm.sec^{-1}$)
3.67_6	4.00_6	0.59_9	1.91_6	-4.23_5	5.81_7

Electrode reaction

As the value of βn found is 0.59, n=1.2 with β = 0.5, which must be an integer. Thus one would conclude that n=1. This value has further been checked by plotting the first derivative polarogram $\Delta i/\Delta E$ vs. E which shows only one peak. With this value of n, the first step reaction can be presumed as:

$$\left[W^{IV}O_2(CN)_4\right]^{4-} \longrightarrow \left[W^{V}O_2(CN)_4\right]^{3-} + e.$$

Thus, the overall electrode reaction may be described as:

$$\left[W^{IV}O_2(CN)_4\right]^{4-} \longrightarrow W^{4+} + 4CN^- + 2O^{2-}$$

$$\left[W^{IV}O_2(CN)_4\right]^{4-} \xrightarrow{e} \left[W^{V}O_2(CN)_4\right]^{3-} \xrightarrow{e} \left[W^{VI}O_2(CN)_4\right]^{2-}$$

in which no chemical reaction seems to be appreciably involved at this temperature. Thus, throughout the oxidations, the complex is considered not to undergo any structural change.

The $\left[W^{IV}O_2(CN)_4\right]^{4-}$ ion is hexacoordinated[6,7] with the electronic structure[16]

$$d^2d^0d^0\left[D^2SP^3\right].$$

On the basis of atomic orbital method[17] the electron transfer mechanism at the electrode surface may be given as:

$$d^2d^0d^0\left[D^2SP^3\right] \xrightarrow{-e} d^1d^0d^0\left[D^2SP^3\right] \xrightarrow{-e} d^0d^0d^0\left[D^2SP^3\right].$$

ACKNOWLEDGEMENTS

The authors are thankful to Professor Wasiur Rahman for providing research facilities.

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